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**For: PROCESS FOR PREPARING MICROENCAPSULATED PIGMENT,  
MICROENCAPSULATED PIGMENT, AQUEOUS DISPERSION, AND INK FOR  
INK JET RECORDING**

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**STATEMENT UNDER 37 C.F.R. 1.55**

Sir,

I, Katsuya TAKENAKA, hereby declare that I am conversant with both English and Japanese languages, and certify to best of my knowledge and belief that the attached is a true and correct English translation of Japanese Patent Application No. 2003-044642 filed in the Japanese Patent and Trademark Office on February 21, 2003 in the Japanese language.

Katsuya TAKENAKA

Date: March 19, 2007

[Designation of Document] SPECIFICATION

[Title of the Invention] PROCESS FOR PREPARING  
MICROENCAPSULATED PIGMENT, MICROENCAPSULATED PIGMENT,  
AQUEOUS DISPERSION, AND INK FOR INK JET RECORDING

[Claims]

[Claim 1] A process for preparing a microencapsulated pigment, the process comprising adding a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a polymerization initiator, and an aqueous medium to a wet pigment, and conducting emulsion polymerization to encapsulate pigment particles with a polymer.

[Claim 2] A process for preparing a microencapsulated pigment, the process comprising adding a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a comonomer copolymerizable with the polymerizable surfactant, a polymerization initiator and an aqueous medium to a wet pigment, and conducting emulsion polymerization to encapsulate pigment particles with a copolymer.

[Claim 3] The process according to claim 2, wherein the comonomer is a hydrophilic monomer and/or a hydrophobic monomer.

[Claim 4] The process according to claim 3, wherein the hydrophobic monomer has at least a hydrophobic group

and a polymerizable group in its structure, and the hydrophobic group is selected from the group consisting of aliphatic hydrocarbon groups, alicyclic hydrocarbon groups, and aromatic hydrocarbon groups.

[Claims 5] The process according to claim 3, wherein the hydrophilic monomer has at least a hydrophilic group and a polymerizable group in its structure, and the hydrophilic group is selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, salts of these groups, a hydroxyl group, an oxyethylene group, an amido group, and an amino group.

[Claim 6] The process according to any one of claims 2 to 5, wherein the polymerizable group of the comonomer is a radically polymerizable unsaturated hydrocarbon group selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group, and a vinylene group.

[Claim 7] The process according to any one of claims 1 to 6, wherein the pigment constituting the pigment particles is carbon black or an organic pigment.

[Claim 8] The process according to any one of claims 1 to 7, wherein the polymerizable group of the polymerizable surfactant is a group selected from the group consisting of a vinyl group, an allyl group, an

acryloyl group, a methacryl group, a propenyl group, a vinylidene group, and a vinylene group.

[Claim 9] The process according to any one of claims 1 to 8, wherein the hydrophilic group of the polymerizable surfactant is an anionic group selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, and salts of these groups, and/or a nonionic group selected from the group consisting of a hydroxyl group, and an oxyethylene group.

[Claim 10] The process according to any one of claims 1 to 9, wherein the hydrophobic group of the polymerizable surfactant is a group selected from the group consisting of alkyl groups, aryl groups, and combinations thereof.

[Claim 11] A microencapsulated pigment obtained by using the process according to any one of claims 1 to 10.

[Claim 12] The microencapsulated pigment according to claim 11, wherein an aspect ratio of the microencapsulated pigment is in the range of 1.0 to 1.3 and a Zingg index thereof is in the range of 1.0 to 1.3.

[Claim 13] An aqueous dispersion containing the microencapsulated pigment according to claim 11 or 12.

[Claim 14] An ink for ink jet recording containing the aqueous dispersion according to claim 13.

[Claim 15] An ink for ink jet recording containing



at least the microencapsulated pigment according to claim 11 or 12 and water.

[Claim 16] The ink for ink jet recording according to any one of claims 14 or 15, further containing a water-soluble organic solvent.

[Claim 17] The ink for ink jet recording according to claim 16, wherein the water-soluble organic solvent is a high boiling water-soluble organic solvent having a boiling point of 180°C or higher.

[Claim 18] The ink for ink jet recording according to claim 16 or 17, wherein the water-soluble organic solvent contains at least one compound selected from the group consisting of glycerol, an alkyl ether of a polyhydric alcohol, and an 1,2-alkyldiol.

[Claim 19] The ink for ink jet recording according to any one of claims 14 to 18, further containing a solid wetting agent in an amount of 3% to 20% by weight based on the total weight of the ink for ink jet recording.

[Claim 20] The ink for ink jet recording according to claim 19, wherein the solid wetting agent is trimethylol propane and/or 1,2,6-hexanetriol.

[Claim 21] The ink for ink jet recording according to any one of claims 14 to 20, further containing a surfactant.

[Claim 22] The ink for ink jet recording according

to claim 21, wherein the surfactant is an acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant.

[Claim 23] The ink for ink jet recording according to any one of claims 14 to 22, further containing a saccharide.

#### [Detailed Description of the Invention]

[0001]

#### [Technical Field to which the Invention belongs]

The present invention relates to a process of preparing a microencapsulated pigment, a microencapsulated pigment, an aqueous dispersion, and an ink for ink jet recording.

[0002]

#### [Prior Art]

An ink jet recording process is a process comprising ejecting ink droplets from a fine nozzle head to form letters or figures on a surface of a recording medium such as paper. As the ink jet recording process, there has been put to practical use a process in which electric signals are converted to mechanical signals with an electrostrictive element, thereby intermittently ejecting ink droplets stored in a nozzle head section to record letters or symbols on a surface of a recording medium, a

process in which a part of an ink solution is rapidly heated at a portion close to an ejection portion of a nozzle head to generate bubbles, and ink droplets are intermittently ejected by volume expansion due to the bubbles to record letters or symbols on a surface of a recording medium, or the like.

[0003]

As an ink for ink jet recording, there has recently been provided an aqueous pigment ink in which a pigment is dispersed in water. This is because an ink using a pigment is characterized by excellent water resistance and light resistance, compared to an ink using a water-soluble dye. In such an aqueous pigment ink, it has been generally carried out that the pigment is dispersed in an aqueous dispersing medium with a dispersant such as a surfactant or a polymer dispersant.

In a pigment ink using an acetylene glycol-based penetrant, it has been studied to use a polymer dispersant as the dispersant for pigment particles, and water, a non-volatile organic solvent or a lower alcohol as the aqueous medium, thereby securing dispersion stability thereof (for example, see patent document 1). However, when the dispersant is used for dispersion of the pigment particles as described above, elements in ink preparation are increased, which makes it difficult to set ink physical

properties such as viscosity to desired values. Further, also in this pigment ink, the problem that print density is difficult to be secured is not solved yet.

Furthermore, in the aqueous pigment ink, the dispersant is merely adsorbed on surfaces of the pigment particles. Accordingly, when the ink solution is ejected through fine nozzles of a recording head, strong shear force is applied thereto, so that the dispersant adsorbed on the surfaces of the pigment particles is eliminated to deteriorate dispersibility, resulting in recognition of the tendency of ejection to become unstable in some cases. Moreover, when the above-mentioned aqueous pigment ink is stored for a long period of time, the tendency of ejection to become unstable is also recognized in some cases.

[0004]

As another technique for dispersing pigment particles in water, there has been proposed a technique of introducing a sulfonic acid group onto a surface of the pigment particle. A pigment ink has been known which contains a surface-sulfonated organic pigment obtained by treating with a sulfonating agent an organic pigment dispersed in an active proton-free solvent (related art 1; for example, see patent document 2). According to related art 1, it has been said that the above-mentioned pigment ink has excellent dispersion stability, and good ejection

stability from the nozzles of the recording head (the characteristic of being stably ejected from the recording head to a definite direction).

Further, it has been known that an organic pigment mass whose surface is positively chargeable is prepared by treating a sulfonic acid group-introduced organic pigment mass with a monovalent metallic ion. Furthermore, there have been known an aqueous ink composition excellent in storage stability (dispersion stability) containing fine pigment particles prepared from the organic pigment mass whose surface is positively chargeable, a dispersant and water (related art 2; for example, see patent document 3).

[0005]

However, although an ink using the surface-treated pigment particles of the above-mentioned related art 1 or related art 2 as a colorant is excellent in dispersion stability and ejection stability, compared to conventional pigment-based inks for ink jet recording, abrasion resistance of recorded matter obtained by printing on a recording medium such as plain paper or a recording medium for ink jet recording (a recording medium having provided on a surface thereof an ink receiving layer for receiving an ink for ink jet recording) has still been insufficient. This is considered to be due to insufficient fixability of the above-mentioned surface-treated pigment particles to

the recording medium.

[0006]

On the other hand, in order to improve fixability of a pigment contained in a pigment-based ink jet recording ink to a recording medium, a technique using a microencapsulated pigment in which a colorant particles are encapsulated with a polymer has been known (for example, see patent documents 4 to 36). Encapsulated fine pigment particles are known in patent documents 4 and 5, and pigment particles in which a polymer is graft polymerized on surfaces thereof are known in patent documents 6 to 9. Patent document 10 proposes a method for microencapsulating a hydrophobic powder with an amphiphilic graft polymer. However, the use of a previously polymerized polymer in microencapsulating has raised the problem that the particle size after encapsulation becomes too large. Patent documents 11 to 19 propose inks containing pigments encapsulated with resins having film forming properties at room temperature by phase reversal of emulsion, and patent documents 20 to 29 propose inks using pigments encapsulated with anionic group-containing organic polymer compounds by acid precipitation.

[0007]

Further, patent documents 30 to 35 propose inks

using polymer emulsions in which fine polymer particles are impregnated with colorants by phase reversal of emulsion (related art 3). However, in the colorant obtained by phase reversal of emulsion or acid precipitation, the polymer adsorbed on the pigment particles is also sometimes eliminated and dissolved in the ink, depending on the kind of organic solvent such as a penetrant used in the ink, so that dispersion stability and ejection stability of the ink, image quality and the like have been insufficient in some cases. In the ink of related art 3, the polymer adsorbed on the pigment particles is not a little eliminated, so that the pigment content in the ink is limited from the point of dispersion stability.

[0008]

Further, in patent document 36, a technique is known in which a polymerizable surfactant and an aqueous medium are added to pigment particles to prepare an emulsion of the pigment particles, and the polymerizable surfactant is polymerized to microencapsulate the pigment particles (related art 4). However, also in this case, dispersion stability and ejection stability of the ink, image quality and the like are still insufficient, so that the pigment content in the ink is limited from the point of dispersion stability.

[0009]

From the above, images of recorded matter obtained by using the inks in which the microencapsulated pigments of related art 3 and related art 4 are used as the colorants have low print density. In particular, when plain paper is used as the recording medium, there have been the problems that blurring is liable to occur in images, and that color developability is also low.

[0010]

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 3-157464

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 10-110129

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 11-49974

[Patent Document 4] Japanese Examined Patent Application Publication No. 7-94634 B

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 8-59715

[Patent Document 6] Japanese Unexamined Patent Application Publication No. 5-339516

[Patent Document 7] Japanese Unexamined Patent Application Publication No. 8-302227

[Patent Document 8] Japanese Unexamined Patent Application Publication No. 8-302228



[Patent Document 9] Japanese Unexamined Patent  
Application Publication No. 8-81647

[Patent Document 10] Japanese Unexamined Patent  
Application Publication No. 5-320276

[Patent Document 11] Japanese Unexamined Patent  
Application Publication No. 8-218015

[Patent Document 12] Japanese Unexamined Patent  
Application Publication No. 8-295837

[Patent Document 13] Japanese Unexamined Patent  
Application Publication No. 9-3376

[Patent Document 14] Japanese Unexamined Patent  
Application Publication No. 8-183920

[Patent Document 15] Japanese Unexamined Patent  
Application Publication No. 10-46075

[Patent Document 16] Japanese Unexamined Patent  
Application Publication No. 10-292143

[Patent Document 17] Japanese Unexamined Patent  
Application Publication No. 11-80633

[Patent Document 18] Japanese Unexamined Patent  
Application Publication No. 11-349870

[Patent Document 19] Japanese Unexamined Patent  
Application Publication No. 2000-7961

[Patent Document 20] Japanese Unexamined Patent  
Application Publication No. 9-31360

[Patent Document 21] Japanese Unexamined Patent  
Application Publication No. 9-217019

[Patent Document 22] Japanese Unexamined Patent  
Application Publication No. 9-316353

[Patent Document 23] Japanese Unexamined Patent  
Application Publication No. 9-104834

[Patent Document 24] Japanese Unexamined Patent  
Application Publication No. 9-151342

[Patent Document 25] Japanese Unexamined Patent  
Application Publication No. 10-140065

[Patent Document 26] Japanese Unexamined Patent  
Application Publication No. 11-152424

[Patent Document 27] Japanese Unexamined Patent  
Application Publication No. 11-166145

[Patent Document 28] Japanese Unexamined Patent  
Application Publication No. 11-199783

[Patent Document 29] Japanese Unexamined Patent  
Application Publication No. 11-209672

[Patent Document 30] Japanese Unexamined Patent  
Application Publication No. 9-286939

[Patent Document 31] Japanese Unexamined Patent  
Application Publication No. 2000-44852

[Patent Document 32] Japanese Unexamined Patent  
Application Publication No. 2000-53897

[Patent Document 33] Japanese Unexamined Patent  
Application Publication No. 2000-53898

[Patent Document 34] Japanese Unexamined Patent  
Application Publication No. 2000-53899

[Patent Document 35] Japanese Unexamined Patent  
Application Publication No. 2000-53900

[Patent Document 36] Japanese Unexamined Patent  
Application Publication No. 10-316909

[0011]

[Problems that the Invention is to Solve]

The invention has been made in view of the above-mentioned problems, and an object of the invention is to provide a process for preparing a microencapsulated pigment, a microencapsulated pigment, and an aqueous dispersion which are capable of preparing an ink for ink jet recording satisfying all the following (1) to (6):

(1) Excellent in dispersion stability;

(2) Excellent in ejection stability from a recording head;

(3) Capable of obtaining recorded matter excellent in fastness of images;

(4) Capable of obtaining recorded matter excellent in print density of images;

(5) Capable of obtaining recorded matter excellent in abrasion resistance of images; and

(6) Capable of obtaining recorded matter in which images are hard to blur, and which is excellent in color developability of images, even when plain paper is used as a recording medium.

Another object of the invention is to provide an ink for ink jet recording satisfying all the above-mentioned (1) to (6).

[0012]

[Means for Solving the Problems]

As a result of extensive studies, the present inventors have discovered that an ink for ink jet recording satisfying all the above-mentioned (1) to (6) can be surprisingly obtained by preparing a specific microencapsulated pigment, and using the microencapsulated pigment as a colorant for the ink for ink jet recording, thus having completed the invention. That is, technical constitution of the invention is as follows.

[0013]

[1] A process for preparing a microencapsulated pigment, which comprises adding a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a polymerization initiator and an aqueous medium to a wet pigment, and conducting emulsion polymerization to encapsulate pigment particles with a polymer.

[2] A process for preparing a microencapsulated pigment, which comprises adding a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a comonomer copolymerizable with the above-mentioned polymerizable surfactant, a polymerization initiator and an aqueous medium to a wet pigment, and conducting emulsion polymerization to encapsulate pigment particles with a copolymer.

[3] The process described in the above [2], wherein the above-mentioned comonomer is a hydrophilic monomer and/or a hydrophobic monomer.

[4] The process described in the above [3], wherein the above-mentioned hydrophobic monomer has at least a hydrophobic group and a polymerizable group in its structure, and the hydrophobic group is selected from the group consisting of aliphatic hydrocarbon groups, alicyclic hydrocarbon groups and aromatic hydrocarbon groups.

[5] The process described in the above [3], wherein the above-mentioned hydrophilic monomer has at least a hydrophilic group and a polymerizable group in its structure, and the hydrophilic group is selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, salts of these groups, a hydroxyl group, an oxyethylene group, an amido

group and an amino group.

[0014]

[6] The process described in any one of the above [2] to [5], wherein the polymerizable group of the above-mentioned comonomer is a radically polymerizable unsaturated hydrocarbon group selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group.

[7] The process described in any one of the above [1] to [6], wherein the pigment constituting the above-mentioned pigment particles is carbon black or an organic pigment.

[8] The process described in any one of the above [1] to [7], wherein the polymerizable group of the above-mentioned polymerizable surfactant is a group selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group.

[9] The process described in any one of the above [1] to [8], wherein the hydrophilic group of the above-mentioned polymerizable surfactant is an anionic group selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group and salts of these groups, and/or a nonionic group

selected from the group consisting of a hydroxyl group and an oxyethylene group.

[0015]

[10] The process described in any one of the above [1] to [9], wherein the hydrophobic group of the above-mentioned polymerizable surfactant is a group selected from the group consisting of alkyl groups, aryl groups and combinations thereof.

[11] A microencapsulated pigment obtained by using the process described in any one of the above [1] to [10].

[12] The microencapsulated pigment described in the above [11], which has an aspect ratio of 1.0 to 1.3, and a Zingg index of 1.0 to 1.3.

[13] An aqueous dispersion containing the microencapsulated pigment described in the above [11] or [12].

[0016]

[14] An ink for ink jet recording containing the aqueous dispersion described in the above [13].

[15] An ink for ink jet recording containing at least the microencapsulated pigment described in the above [11] or [12] and water.

[16] The ink for ink jet recording according to any one of the above [14] or [15], further containing a water-soluble organic solvent.

[17] The ink for ink jet recording described in the above [16], wherein the water-soluble organic solvent is a high boiling water-soluble organic solvent having a boiling point of 180°C or higher.

[18] The ink for ink jet recording described in the above [16] or [17], wherein the water-soluble organic solvent contains at least one compound selected from the group consisting of glycerol, an alkyl ether of a polyhydric alcohol, and an 1,2-alkyldiol.

[19] The ink for ink jet recording described in any one of the above [14] to [18], further containing a solid wetting agent in an amount of 3% to 20% by weight based on the total weight of the ink for ink jet recording.

[0017]

[20] The ink for ink jet recording described in the above [19], wherein the solid wetting agent is trimethylolpropane and/or 1,2,6-hexanetriol.

[21] The ink for ink jet recording described in any one of the above [14] to [20], further containing a surfactant.

[22] The ink for ink jet recording described in the above [21], wherein the surfactant is an acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant.

[23] The ink for ink jet recording described in any



one of the above [14] to [22], further containing a saccharide.

[0018]

[Mode for Carrying out the Invention]

The process for preparing a microencapsulated pigment according to the invention is characterized in that a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a polymerization initiator and an aqueous medium are added to a wet pigment, and pigment particles are encapsulated with a polymer by conducting emulsion polymerization.

Further, the process for preparing a microencapsulated pigment according to the invention is characterized in that a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a comonomer copolymerizable with the above-mentioned polymerizable surfactant, a polymerization initiator and an aqueous medium are added to a wet pigment, and pigment particles are encapsulated with a copolymer by conducting emulsion polymerization.

[0019]

According to such a preparation process, the hydrophobic group of the polymerizable surfactant is adsorbed on a hydrophobic surface of the pigment particle of the wet pigment by a hydrophobic interaction to bring

about a state in which the hydrophilic group is directed toward a direction in which the aqueous medium exists, that is, toward an aqueous phase side. The hydrophilic group can be introduced onto the surface of the pigment particle in a highly controlled form by conducting a polymerization reaction with the polymerization initiator in this state. Further, also when the comonomer is used, the hydrophilic groups are regularly densely orientated toward a direction in which the aqueous medium exists, that is, toward an aqueous phase side, and a comonomer-derived polymer layer is formed between the pigment particle and the hydrophilic group derived from the polymerizable surfactant, which makes it possible to form a highly controlled capsule structure. Accordingly, the microencapsulated pigment according to an embodiment of the invention is capable of preparing an ink for ink jet recording satisfying all the following (1) to (6):

- (1) Excellent in dispersion stability;
- (2) Excellent in ejection stability from a recording head;
- (3) Capable of obtaining recorded matter excellent in fastness of images;
- (4) Capable of obtaining recorded matter excellent in print density of images;

(5) Capable of obtaining recorded matter excellent in abrasion resistance of images; and

(6) Capable of obtaining recorded matter in which images are hard to blur, and which is excellent in color developability of images, even when plain paper is used as a recording medium. In the case of a microencapsulated pigment in which a pigment is encapsulated with a polymer previously prepared by phase reversal of emulsion or acid precipitation, a state of pigment particles encapsulated with the polymer is determined by the structure of the polymer. It is therefore considered that such a state of pigment particles encapsulated with the polymer that all the above-mentioned (1) to (6) are satisfied has not been achieved.

[0020]

Here, it is preferred that the microencapsulated pigment of the invention has an aspect ratio (long-short degree) of 1.0 to 1.3, and a Zingg index of 1.0 to 1.3 (more preferably 1.0 to 1.2), thereby being able to satisfy the above-mentioned (1), (2), (4) and (6) more securely.

When the minor diameter, major diameter and thickness of a particle are taken as  $b$ ,  $l$  and  $t$  ( $l \geq b \geq t > 0$ ), respectively, the aspect ratio (long-short degree) is  $l/b$  ( $\geq 1$ ), the degree of flatness is  $b/t$  ( $\geq 1$ ), and the Zingg

index is the long-short degree/the degree of flatness =  $(1-t)/b^2$ . That is, the true sphere has an aspect ratio of 1 and a Zingg index of 1.

When the aspect ratio is larger than 1.3, the microencapsulated pigment becomes flatter in shape to lower the isotropy. This perhaps accounts for the fact that there is a tendency to fail to obtain sufficient results, particularly with respect to the above (1), (2), (4) and (6). Although there is no particular limitation on the method for adjusting the aspect ratio and the Zingg index within the above-mentioned ranges, the aspect ratio and the Zingg index can be adjusted more securely within the above-mentioned ranges by using methods according to embodiments of the invention described later. As for microencapsulated pigments prepared by methods other than emulsion polymerization, such as acid precipitation and phase reversal of emulsion, it is difficult to adjust the aspect ratio and the Zingg index within the above-mentioned ranges.

[0021]

When the microencapsulated pigment is in the range of aspect ratio and Zingg index, the pigment particles have the shape of a true sphere. Accordingly, an ink using the microencapsulated pigment easily becomes Newtonian in its fluid characteristics and is thus

excellent in ejection stability of the ink. Further, the microencapsulated pigment particles shaped like a true sphere are arranged at a high density on a recording medium such as paper to reproduce the printing concentration and the color with high efficiency, when the ink lands on the recording medium. Further, the true sphere-shaped pigment particles exhibit excellent dispersibility or dispersion stability.

[0022]

The invention will be described in detail below, with reference to dispersed states of the pigment particles which can occur in the method for preparing the microencapsulated pigment. The dispersed states of the pigment particles described below include assumptions.

[0023]

Fig. 1 is a view showing a state in which pigment particle 1 is dispersed in a solvent containing water as a main component (hereinafter also referred to as an aqueous medium), and coexists with a polymerizable surfactant 2 having a hydrophilic group 11, a hydrophobic group 12 and a polymerizable group 13. A surface 50 of the pigment particle 1 forms a hydrophobic region herein. The polymerizable surfactant 2 is adsorbed so that the hydrophobic group 12 is directed toward the pigment particle 1 by an interaction of the hydrophobic group 12

with the hydrophobic region 50. The hydrophilic group 11 of the polymerizable surfactant 2 is directed toward a direction in which the aqueous medium exists, that is, a direction departing from the pigment particle 1.

[0024]

To such an aqueous dispersion, for example, a polymerization initiator is added to polymerize the polymerizable groups 13 of the polymerizable surfactant 2, thereby preparing a microencapsulated pigment 100 in which the pigment particle 1 is encapsulated with a polymer layer 60, as shown in Fig. 2. A surface of the polymer layer 60 has the hydrophilic group 11, so that the microencapsulated pigment 100 is dispersible in the aqueous medium. At the time of polymerization, a comonomer copolymerizable with the polymerizable surfactant 2 may be allowed to exist in the aqueous dispersion as needed. In that case, the polymer layer 60 can be a copolymer layer copolymerized from the polymerizable surfactant 2 and the comonomer.

[0025]

The dispersed states have been described with reference to the drawings. The pigment particles 1 are dispersed in the aqueous medium by arranging the polymerizable surfactant 2 around the pigment particles. In that a wet pigment is used in the pigment particles 1

in the aqueous medium, the pigment particles 1 are finely dispersible compared to an aqueous dispersion in which a dry powder of a pigment is used. According to such a microencapsulated pigment of the embodiment in which the pigment particles having the hydrophilic group on the surface thereof are encapsulated with the polymer, since the hydrophilic groups on the surface of the microencapsulated pigment are regularly densely orientated in a direction in which the aqueous medium exists as shown in Fig. 2, it is possible to enhance the dispersion stability of the microencapsulated pigment in the aqueous medium. Accordingly, by using the microencapsulated pigment of the invention as a colorant of the ink for ink jet recording and using an aqueous medium as the solvent of the ink, even when a more weight of microencapsulated pigment is contained in the ink, it is possible to obtain the same dispersion stability as a conventional microencapsulated pigment. When the dispersion stability is excellent, there is reduced the possibility that the microencapsulated pigment clog a nozzle of a recording head, thereby improving the ejection stability. That is, it is possible to prepare an ink of the microencapsulated pigment, which is excellent in dispersion stability and ejection stability and which has an weighted concentration of the colorant compared to a conventional

microencapsulated pigment ink. Further, by performing an ink jet recording operation using the ink of the microencapsulated pigment having the high weighted concentration of the colorant, it is possible to obtain printed matters having high-rigidity images and having high-print-density images.

[0026]

More specifically, in the microencapsulated pigment of the invention, as described above, since the hydrophilic groups derived from the polymerizable surfactant are regularly densely oriented toward the aqueous medium, it is considered that effective electrostatic repulsion occurs between the microencapsulated pigment particles. In addition to the electrostatic repulsion, it is considered that an effect (polymer effect) of spatial disturbance resulting from a copolymer of a homopolymer or comonomer of the polymerizable surfactant encapsulating the pigment particles is one reason for the excellent dispersion stability of the microencapsulated pigment of the invention in the aqueous medium.

[0027]

When plain paper is used as the recording medium, blurring is hard to occur in printed images, and the print density of images is also high. The reason for this is



considered to be largely due to that the hydrophilic groups existing on the surface of the microencapsulated pigment are regularly densely orientated toward the aqueous medium. Usually, when the ink is ejected from the recording head and lands on the plain paper, the aqueous medium rapidly penetrates into the plain paper, but the pigment particles of the conventional pigment ink using the pigment particles dispersed with a dispersant (the pigment particles are coated with the dispersant) also move into the paper together with the aqueous medium and the pigment particles are difficult to be adsorbed on cellulose fiber on a print surface of the plain paper (this is because the amount of the hydrophilic groups on the pigment surface is smaller than that of the microencapsulated pigment according to the invention and the hydrophilic groups are not regularly densely oriented), so that the print density is low, and the color developability also become insufficient.

In contrast, the microencapsulated pigment of the invention easily agglomerates by an interaction of the hydrophilic groups (particularly, the anionic groups) existing on the surface of the microencapsulated pigment with various metallic ions such as magnesium, calcium, and aluminum usually contained in the plain paper, or can be easily adsorbed and agglomerates by an interaction of the

hydrophilic groups (particularly, the anionic groups) of the microencapsulated pigment with cationic starch and a cationic polymer used together with a sizing agent in sizing treatment of the plain paper. Further, the microencapsulated pigment is easily adsorbed on a surface of the cellulose fiber by an interaction of the hydrophilic groups (particularly, the anionic groups) with the cellulose fiber. Accordingly, when ink droplets using the microencapsulated pigment of the invention as the colorant are ejected from the recording head and land on the plain paper, the colorant is easily collected in the vicinity of a landing position on the plain paper. Therefore, it is considered that it is possible to high image density and to suppress blurring from occurring.

[0028]

Since the pigment particles are coated with the polymer, the ink for ink jet recording according to the invention has excellent fixability to the recording medium and excellent abrasion resistance of the recorded matter, compared with the conventional ink using surface-treated pigment particles as the colorant.

[0029]

Constituents used in the process for preparing a microencapsulated pigment of the invention will be described in detail below.

[0030]

Preferable examples of the pigments preferably used in the invention include the following inorganic pigments and organic pigments.

The inorganic pigments include carbon blacks (C.I. Pigment Black 7) such as furnace black, lamp black, acetylene black and channel black, and an iron oxide pigment. As the organic pigments, there can be used an azo pigment (including azo lake, an insoluble azo pigment, a condensed azo pigment and a chelate azo pigment), a polycyclic pigment (for example, a phthalocyanine pigment, a perylene pigment, a perinone pigment, an anthraquinone pigment, a quinacridone pigment, a dioxane pigment, a thioindigo pigment, an isoindolinone pigment or a quinofranone pigment), a dye chelate (for example, a basic dye chelate or an acidic dye chelate), a nitro pigment, a nitroso pigment or aniline black.

[0031]

More specifically, the inorganic pigments used for black include carbon blacks such as No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100 and No. 2200B manufactured by Mitsubishi Chemical Corporation, Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255 and Raven 700 manufactured by Columbian Chemicals Company, Regal 400R, Regal 330R, Regal 660R, Mogul L, Monarch 700,

Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300 and Monarch 1400 manufactured by Cabot Corporation, and Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, Printex 35, Printex U, Printex V, Printex 140U, Special Black 6, Special Black 5, Special Black 4A and Special Black 4 manufactured by Degussa Corporation.

Further, as the organic pigments for black, there can be used black organic pigments such as aniline black (C.I. Pigment Black 1).

[0032]

Still further, the organic pigments for yellow inks include C.I. Pigment Yellow 1 (hansa yellow), 2, 3 (hansa yellow 10G), 4, 5 (hansa yellow 5G), 6, 7, 10, 11, 12, 13, 14, 16, 17, 24 (flavanthrones Yellow), 34, 35, 37, 53, 55, 65, 73, 74, 75, 81, 83, 93, 94, 95, 97, 98, 99, 108 (anthrapyrimidine yellow), 109, 110, 113, 117 (copper complex pigment), 120, 124, 128, 129, 133 (quinophthalones), 138, 139 (isoindolinones), 147, 151, 153 (nickel complex pigment), 154, 167, 172, and 180.

[0033]

Yet still further, the organic pigments for magenta inks include C.I. Pigment Reds 1 (para red), 2, 3 (toluidine red), 4, 5 (1TR red), 7, 8, 9, 10, 11, 12, 14,

15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38  
(pyrazolone red), 40, 41, 42, 48 (Ca), 48 (Mn), 57 (Ca),  
57:1, 88 (thioindigo), 112 (naphthol AS), 114 (naphthol  
AS), 122 (dimethyl quinacridone), 123, 144, 146, 149, 150,  
166, 168 (antianthrone organe), 170 (naphthol AS), 171,  
175, 176, 177, 178, 179 (perylene marun), 184, 185, 187,  
202, 209 (dichloroquinacridone), 219, 224 (perylene), and  
245 (naphthol AS), and C.I. Pigment Violet 19  
(quinacridone), 23 (dioxadine violet), 32, 33, 36, 38, 43  
and 50.

[0034]

Furthermore, the organic pigments for cyan inks  
include C.I. Pigment Blue 1, 2, 3, 15, 15:1, 15:2, 15:3,  
15:34, 15:4, 16 (nonphthalocyanine), 18 (alkali blue  
toner), 22, 25, 60 (threne blue), 65 (violanthrone), and  
66 (Indigo), and C.I. Vat Blue 4 and 60.

[0035]

In addition, as the organic pigments used for color  
inks other than magenta, cyan, and yellow inks, there can  
be used C.I. Pigment Green 7 (phthalocyanine green), 10  
(green gold), 36, and 37; C.I. Pigment Brawn 3, 5, 25, and  
26; and C.I. Pigment Orange 1, 2, 5, 7, 13, 14, 15, 16, 24,  
34, 36, 38, 40, 43 and 63.

[0036]

The aqueous dispersion of the pigment particles

including the above-described pigment is obtained by dispersing the "wet pigment" obtained from the process of preparing the pigment in the aqueous medium. The "wet pigment" contains water of 40 to 80% by weight without drying the liquid-phase pigment (see Japanese Unexamined Patent Application Publication Nos. 9-288378 and 9-288379). Usually, agglomeration of the pigment particles proceeds with a decrease in water content to increase the particle size of the pigment, thereby making the dispersion insufficient. In general, a pigment is synthesized through various reactions, and finally dried to form a powder. The "wet pigment" used in the invention is a pigment containing water before drying. Examples of the wet pigments include the followings. Examples of the pigments constituting the wet pigment include various wet pigments such as organic pigments such as a Monoazo Yellow pigment, a Disazo Yellow pigment, a carmine pigment, a rhodamine pigment, a quinacridone pigment, a phthalocyanine pigment, an anthraquinone pigment, a thioindigo pigment, a perinone pigment, a perylene pigment, a dioxane pigment, a quinophthalone pigment, an isoindolinone pigment, and a benzimidazolone pigment, and carbon blacks. In the invention, C.I. Pigment Red 48:1, C.I. Pigment Red 122, C.I. Pigment Yellow 17 and C.I. Pigment Blue 15:3 are particularly preferably used.

[0037]

(1) Azo Pigment

The azo pigment is obtained by the coupling reaction of a diazonium salt with a coupling component (such as a  $\beta$ -naphthol derivative showing keto-enol type tautomerism, an acetoacetic acid anilide derivative or a pyrazolone derivative). The coupling reaction is conducted in the presence of an alkali compound, and a solution after the reaction contains an azo pigment, a salt and water. The solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the azo pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0038]

(2) Phthalocyanine Pigment

The phthalocyanine pigment is obtained by conducting a pigmentation process such as a sulfuric acid process (a process for modifying the crystal form, the form of primary particles and the particle size distribution of a crude pigment to develop physical properties as a colorant) to a crude pigment (which is an acicular crystalline material, and cannot be used as it is) obtained by a phthalic anhydride process or a

phthalodinitrile process. As the sulfuric acid processes, there have been known an acid pasting process and an acid slurry process.

In the acid pasting process, the crude pigment is dissolved in sulfuric acid having a concentration of 95% or more, and the resulting solution is poured into a large amount of water to precipitate the phthalocyanine pigment as fine particles. This solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the azo pigment in a wet state with water is also usable as the wet pigment of this embodiment (a wet cake described in JP 9-279052 A, a pigment paste described in JP 2002-265812 A, or the like)

In the acid slurry process, the crude pigment is added to sulfuric acid having a concentration of 60 to 90%, followed by stirring to form crystals of phthalocyanine sulfate, which are poured into a large amount of water to precipitate the phthalocyanine pigment as fine particles. This solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the phthalocyanine pigment in a wet state with water is also usable as the wet pigment of



this embodiment (a pigment cake described in JP 8-217986 A, or the like).

[0039]

(3) Polycyclic Pigment

(3-1) Quinacridone Pigment

As the preparation of the quinacridone pigment, there has been known a process for obtaining it by oxidation of dihydroquinacridone. In this case, the solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the quinacridone pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0040]

(3-2) Isoindolinone Pigment

The isoindolinone pigment is obtained by reacting 1 mole of an isoindolinone derivative with 2 moles of an aromatic diamine. The solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the isoindolinone pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0041]

### (3-3) Perylene Pigment

The perylene pigment is obtained by a process comprising (i) reacting perylenetetracarboxylic acid diimide with sulfuric acid to prepare C.I. Pigment Red 224 (the first step) and then, reacting C.I. Pigment Red 224 with an aniline derivative (the second step), or (ii) reacting perylenetetracarboxylic acid diimide with an alkyl chloride.

In (i), the solution after the first step and a concentrate thereof are usable as the wet pigment (C.I. Pigment Red 224) of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing C.I. Pigment Red 224 in a wet state with water is also usable as the wet pigment of this embodiment. Furthermore, the solution of the second step and a concentrate thereof are usable as the wet pigment of this embodiment. Moreover, a product of the state after filtering the solution after the reaction, and washing the perylene pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0042]

Further, pigment cakes before drying in processes for preparing disazo lake pigments described in Japanese Unexamined Patent Application Publication Nos. 5-9399, 5-9400, 5-65426, 7-126545, and 9-217017 are usable as the

wet pigments of this embodiment.

[0043]

Furthermore, commercially available products usable as the wet pigments in this embodiment include an aqueous Lithol (registered trade mark)-Rubine-pigment suspension (C.I. 15850) and a Heliogen (registered trade mark)-blue-pigment cake (C.I. 74160).

[0044]

In an aqueous dispersion of the microencapsulated pigment of the invention, the use of the wet pigment as described above allows the average particle size of pigment particles to be easily adjusted to 150 nm or less, thereby being able to impart excellent dispersibility, dispersion stability and ejection stability to the ink for ink jet recording using the microencapsulated pigment of the invention, and to increase the print density of images. When a general powder pigment is used, the particle size of the resulting microencapsulated pigment is liable to become large, which causes poor dispersibility, dispersion stability and ejection stability of the ink, and the print density of printed matter tends to decrease (in this specification, the description of the average particle size is described based on measured values by a laser light scattering process).

[0045]

The microencapsulated pigment according to the embodiment of the invention can be suitably prepared by adding the polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, the polymerization initiator and the aqueous medium to the wet pigment, and conducting emulsion polymerization, as described above.

[0046]

The polymerizable surfactant used in the invention will be described below. The hydrophilic group of the polymerizable surfactant used in the invention is preferably an anionic group selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group and salts of these groups, and/or a nonionic group selected from the group consisting of a hydroxyl group and an oxyethylene group, and the hydrophobic group is preferably selected from the group consisting of an alkyl group, an aryl group and a combination thereof. The polymerizable group is preferably an unsaturated hydrocarbon group, and more particularly, one selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group. Of these, an acryloyl group and a methacryloyl group are particularly preferable.

[0047]

Specific examples of the polymerizable surfactants used in the invention include anionic allyl derivatives as described in Japanese Examined Patent Application Publication Nos. 49-46291 and 1-24142 and Japanese Unexamined Patent Application Publication No. 62-104802, anionic propenyl derivatives as described in Japanese Unexamined Patent Application Publication No. 62-221431, anionic acrylic acid derivatives as described in Japanese Unexamined Patent Application Publication Nos. 62-34947 and 55-11525, anionic itaconic acid derivatives as described in Japanese Examined Patent Application Publication No. 46-34898 and Japanese Unexamined Patent Application Publication Nos. 51-30284, anionic maleic acid derivatives as described in Japanese Examined Patent Application Publication No. 51-4157 and Japanese Unexamined Patent Application Publication No. 51-30284, nonionic allyl derivatives as described in Japanese Unexamined Patent Application Publication No. 62-104802, nonionic propenyl derivatives as described in Japanese Unexamined Patent Application Publication No. 62-100502, nonionic acrylic acid derivatives as described in Japanese Unexamined Patent Application Publication No. 56-28208, nonionic itaconic acid derivatives as described in Japanese Examined Patent Application Publication No. 59-

12681, nonionic maleic acid derivatives as described in Japanese Unexamined Patent Application Publication No. 59-74102, and cationic allyl derivatives as described in Japanese Examined Patent Application Publication No. 4-65824.

[0048]

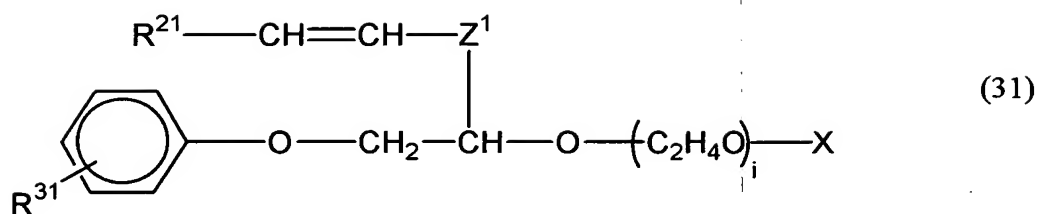
The polymerizable surfactants used in the invention include, for example, an acrylic acid-modified polyoxyethylene alkyl ether, an acrylic acid-modified polyoxyethylene alkyl phenyl ether, an allylic acid-modified polyoxyethylene alkyl ether, an allylic acid-modified polyoxyethylene alkyl phenyl ether, an allylic acid-modified polyoxyethylene polystyrylphenyl ether, an acrylic acid-modified polyoxyethylene polystyrylphenyl ether, and polyoxyethylene-polyoxypropylene glycol monoacrylate.

[0049]

The polymerizable surfactants preferably used in the invention include, for example, a compound represented by general formula (31).

[0050]

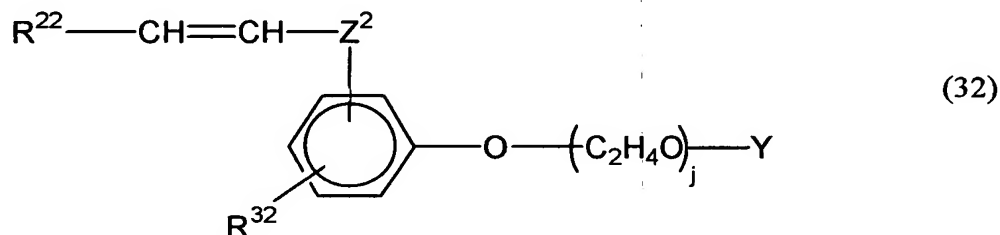
[Kagaku 1]



where  $\text{R}^{21}$  and  $\text{R}^{31}$  are each independently a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms;  $\text{Z}^1$  is a group represented by a carbon-carbon single bond or formula  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ;  $i$  is an integer of 2 to 20; and  $\text{X}$  is a hydrogen atom or formula  $-\text{SO}_3\text{M}^1$ , wherein  $\text{M}^1$  is an alkali metal, an ammonium salt or an alkanolamine; and a compound represented by general formula (32).

[0051]

[Kagaku 2]



[where  $\text{R}^{22}$  and  $\text{R}^{32}$  are each independently a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms;  $\text{Z}^2$  is a group represented by a carbon-carbon single bond or formula  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ;  $j$  is an integer of 2 to 20; and  $\text{Y}$  is a hydrogen atom or formula  $-\text{SO}_3\text{M}^2$ , wherein  $\text{M}^2$  is an alkali metal, an ammonium salt or an alkanolamine.]

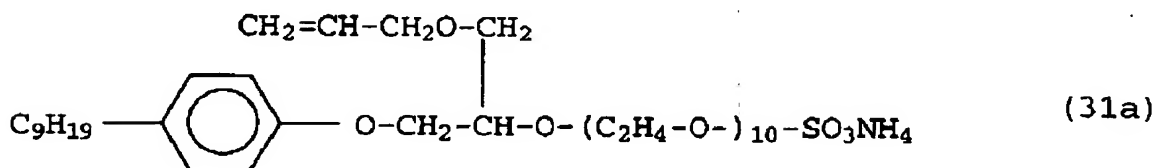
[0052]

The polymerizable surfactants represented by the

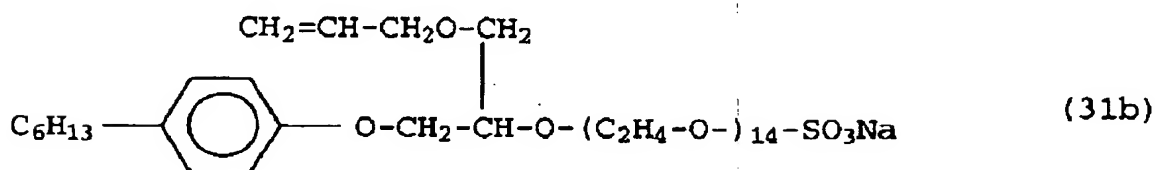
above-mentioned formula (31) are described in JP 5-320276 A and JP 10-316909 A. It is possible to adjust the adsorbability onto the surface of the pigment particle and the hydrophilicity of the surface of the pigment particle by appropriately adjusting the kind of  $R^{21}$  and the value of  $i$ . Preferred specific examples of the polymerizable surfactants represented by formula (31) include compounds represented by the following formulas (31a) to (31d).

[0053]

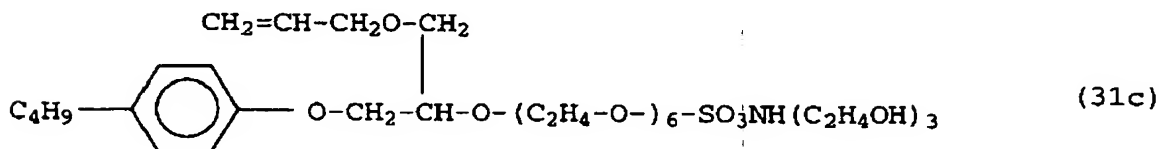
[Kagaku 3]



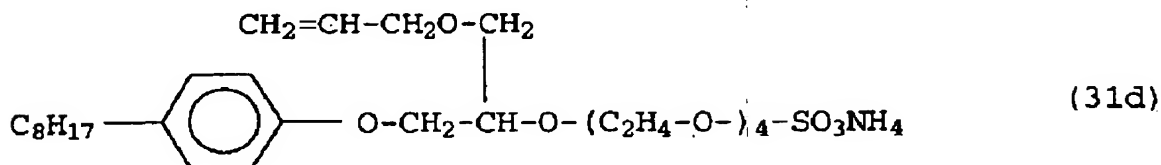
[Kagaku 4]



[Kagaku 5]



[Kagaku 6]





[0054]

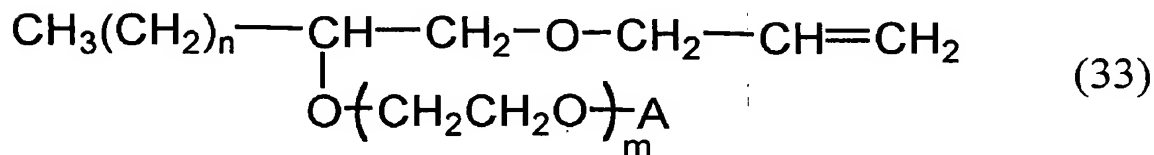
As the above-mentioned polymerizable surfactants, there can also be used commercially available products. Examples thereof include Aqualon HS series (Aqualon HS-05, HS-10, HS-20 and HS-1025), Aqualon RN series (RN-10, RN-20, RN-30, RN-50 and RN-2025) and New Frontier series (New Frontier N-177E and S-510), all of which are supplied from Daiichi Kogyo Yakuhin Co., Ltd.; and Adeka Reasoap SE series (SE-10N) and Adeka Reasoap NE series (NE-5, NE-10, NE-20, NE-30 and NE-40), all of which are supplied from Asahi Denka Co., Ltd.

[0055]

Further, the polymerizable surfactants preferably used in the invention include, for example, a compound represented by general formula (33).

[0056]

[Kagaku 7]

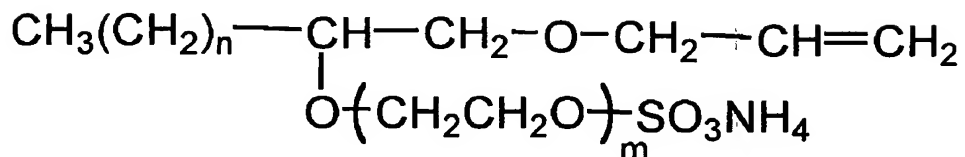


[where n is 9 or 11; m is an integer of 2 to 20; and A is a group represented by a hydrogen atom or  $-\text{SO}_3\text{M}^3$ , wherein  $\text{M}^3$  is an alkali metal, an ammonium salt or an alkanol

amine.] Preferred specific examples of the polymerizable surfactants represented by formula (33) include the following compound.

[0057]

[Kagaku 8]



[where n is 9 or 11; and m is 5 or 10.]

[0058]

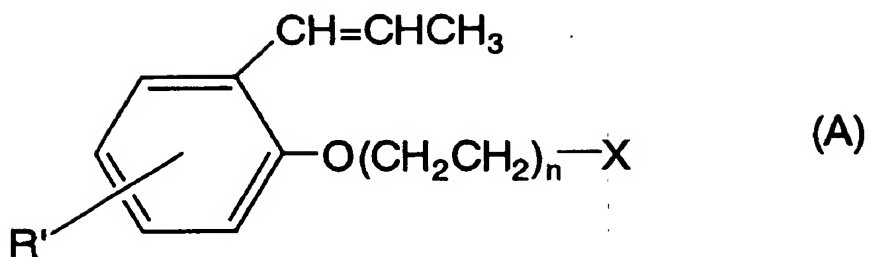
As the above-mentioned polymerizable surfactants, there can also be used commercially available products. Examples thereof include Aqualon KH-05 and Aqualon KH-10 supplied from Daiichi Kogyo Yakuhin Co., Ltd.

[0059]

Further, a compound represented by the following formula (A) is also preferred as the polymerizable surfactant.

[0060]

[Kagaku 9]



$X; -SO_3M, -H$

[where R' represents a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms; n represents a number of 2 to 20; and M represents an alkali metal, an ammonium salt or an alkanolamine.]

[0061]

The polymerizable surfactants exemplified above can be used either alone or as a mixture of two or more thereof.

[0062]

The added amount of the polymerizable surfactant is preferably in the range of 5 to 70% by weight, more preferably within the range of about 10 to 50% by weight, based on the pigment. By adjusting the amount of the surfactant added to 5% by weight or more, the dispersibility of the encapsulated particles is excellent and the ejection stability is also excellent. The adsorbability to paper fiber is improved, thereby

resulting in excellent print density and color developability. Furthermore, the amount of the polymerizable surfactant which makes no contribution to a microencapsulation reaction of the pigment particles can be reduced to inhibit the generation of polymer particles having no pigment particles as a core substance by adjusting the above-mentioned amount of the surfactant added to 70% by weight or less.

[0063]

The microencapsulated pigment can also be suitably produced by mixing the wet pigment, the polymerizable surfactant having a hydrophilic group, a hydrophobic group, and a polymerizable group, a comonomer copolymerizable with the polymerizable surfactant, a polymerization initiator, and an aqueous medium, and conducting emulsion polymerization. Accordingly, the fixability to the recording medium and the abrasion resistance can be controlled and the storage stability of the ink can be controlled. In particular, the fixability to the recording medium and the abrasion resistance can be improved by controlling the glass transition temperature ( $T_g$ ) of a copolymer covering the pigment particles of the microencapsulated pigment according to the invention. The glass transition temperature ( $T_g$ ) is preferably in the range of  $-20^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ . When the glass transition

temperature ( $T_g$ ) exceeds  $30^{\circ}\text{C}$ , the fixability and abrasion resistance tend to decrease. When it is lower than  $-20^{\circ}\text{C}$ , the solvent resistance tends to decrease.

[0064]

The above-mentioned comonomers include a hydrophilic monomer and a hydrophobic monomer.

The hydrophobic monomer used in the invention is one having at least a hydrophobic group and a polymerizable group in its structure, and the hydrophobic group is suitably selected from the group consisting of an aliphatic hydrocarbon group, an alicyclic hydrocarbon group and an aromatic hydrocarbon group. Further, the hydrophilic monomer used in the invention is one having at least a hydrophilic group and a polymerizable group in its structure, and the hydrophilic group is suitably selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, salts of these groups, a hydroxyl group, an oxyethylene group, an amido group and an amino group.

[0065]

The polymerizable group as used herein is a radically polymerizable unsaturated hydrocarbon group, in either case of a hydrophilic monomer or a hydrophobic monomer, and preferably selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a

methacryloyl group, a propenyl group, a vinylidene group and a vinylene group.

[0066]

In the hydrophobic monomers used in the invention, the aliphatic hydrocarbon groups include a methyl group, an ethyl group and a propyl group, the alicyclic hydrocarbon groups include a cyclohexyl group, a dicyclopentenyl group and isobornyl group, and the aromatic hydrocarbon groups include a benzyl group, a phenyl group and a naphthyl group.

[0067]

Further, specific examples of the hydrophobic monomers include styrene derivatives such as styrene,  $\alpha$ -methyl styrene, o-methyl styrene, m-methyl styrene, p-methylstyrene, dimethyl styrene, p-tertbutyl styrene, chlorostyrene, dichloro styrene, bromostyrene and p-chloromethylstyrene; mono-functional acrylic esters such as methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, n-octyl acrylate, lauryl acrylate, dodecyl acrylate, stearyl acrylate, tridecyl acrylate, isodecyl acrylate, isooctyl acrylate, isomyristyl acrylate, isostearyl acrylate, isoamyl acrylate, 2-ethylhexyl acrylate, benzyl acrylate, phenyl acrylate, phenoxyethyl acrylate, phenoxydiethylene glycol acrylate,

phenoxy polyethylene glycol acrylate, ethylene oxide-modified nonylphenol acrylate, cyclohexyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, dicyclopentenyl oxyethyl acrylate, isobornyl acrylate and tetrahydrofurfuryl acrylate; monofunctional methacrylic esters such as methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, isobutyl methacrylate, n-octyl methacrylate, lauryl methacrylate, dodecyl methacrylate, stearyl methacrylate, tridecyl methacrylate, isodecyl methacrylate, isooctyl methacrylate, isomyristyl methacrylate, isostearyl methacrylate, isoamyl methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, phenyl methacrylate, phenoxyethyl methacrylate, phenoxy diethylene glycol methacrylate, phenoxy polyethylene glycol methacrylate, ethylene oxide-modified nonylphenol methacrylate, cyclohexyl methacrylate, dicyclopentanyl methacrylate, dicyclopentenyl methacrylate, dicyclopentenyl oxyethyl methacrylate, isobornyl methacrylate and tetrahydrofurfuryl methacrylate; addition reaction products of oil fatty acids and oxirane structure-containing (meth)acrylic ester monomers such as an addition reaction product of stearic acid and glycidyl methacrylate; addition reaction products of oxirane compounds containing an alkyl group having 3 or more

carbon atoms and (meth)acrylic acid; allyl compounds such as allyl benzene, allyl-3-cyclohexane propanate, 1-allyl-3,4-dimethoxybenzene, allyl phenoxyacetate, allyl phenylacetate and allylcyclohexane; esters of fumaric acid, maleic acid and itaconic acid; and radically polymerizable group-containing monomers such as an N-substituted maleimide and a cyclic olefin.

[0068]

Preferably, the hydrophilic monomer used in the invention is one having at least a hydrophilic group and a polymerizable group in its structure, and the hydrophilic group is suitably selected from the group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, salts of these groups, a hydroxyl group, an oxyethylene group, an amido group and an amino group.

In particular, a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group and salts of these groups easily interact with various metal ions such as magnesium, calcium and aluminum, cationic starch and cationic polymers which are usually contained in plain paper, and also easily interact with a surface of cellulose fiber constituting the plain paper. Accordingly, when the plain paper is printed with the ink for ink jet recording using the microencapsulated pigment produced by



use of the above-mentioned hydrophilic monomer, by the ink jet recording process, the above-mentioned microencapsulated pigment is easy to stay in the vicinity of a landing position. Accordingly, high image density is obtained more reliably, and blurring can also be inhibited from occurring in images.

From such a viewpoint, preferred specific examples of the hydrophilic monomers used in the invention include, for example, acrylic acid, methacrylic acid, propylacrylic acid, isopropylacrylic acid, 2-acryloyloxyethylsuccinic acid, 2-acryloyloxyethylphthalic acid, 2-methacryloyloxyethylsuccinic acid, 2-methacryloyloxyethylphthalic acid, itaconic acid, fumaric acid and maleic acid. Of these, acrylic acid and methacrylic acid are preferred. Further, the sulfonic acid group-containing monomers include, for example, 4-styrenesulfonic acid and a salt thereof, vinylsulfonic acid and a salt thereof, sulfoethyl acrylate and a salt thereof, sulfoethyl methacrylate and a salt thereof, a sulfoalkyl acrylate and a salt thereof, a sulfoalkyl methacrylate and a salt thereof, sulfopropyl acrylate and a salt thereof, sulfopropyl methacrylate and a salt thereof, a sulfoaryl acrylate and a salt thereof, a sulfoaryl methacrylate and a salt thereof, butylacrylamidosulfonic acid and a salt thereof, and 2-

acrylamido-2-methylpropanesulfonic acid and a salt thereof. Still further, phosphone group -containing monomers include a phosphoric acid group-containing (meth)acrylate such as phosphoethyl methacrylate. Yet still further, the hydroxyl group-containing monomers include, for example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxybutyl methacrylate, polyethylene glycol 400 monoacrylate, polyethylene glycol 400 monomethacrylate, polyethylene glycol monomethacrylate, N-hydroxyethyl acrylate, N-hydroxyethyl methacrylate, dipropylene glycol acrylate and 2-hydroxy-3-phenoxypropyl acrylate. Furthermore, the amido group-containing monomers include acrylamide, methacrylamide, acrylaminoethylamide, acrylmethylaminoethylamide, acrylmethyl aminopropylamide, acrylethylaminoethylamide, acrylethyl aminopropylamide, acrylaminoethylamide, methacryl aminoethylamide, methacrylmethylaminoethylamide, methacrylmethyl aminopropylamide, methacrylethyl aminoethylamide, methacrylethyl aminopropylamide, methacrylaminoethylamide and vinylpyrrolidone. Moreover, they include ethyldiethylene glycol acrylate, ethyldiethylene glycol methacrylate, methoxypolyethylene glycol acrylate, methoxyethylene glycol methacrylate, methoxytriethylene glycol methacrylate and N-vinyl-2-

pyrrolidone.

[0069]

Further, a crosslinking monomer can also be used in the invention. The crosslinking monomer usable in the invention is a compound having two or more of unsaturated hydrocarbon groups of at least one kind selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group. Examples thereof include ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol diacrylate, allyl acrylate, bis(acryloxyethyl)hydroxyethyl isocyanurate, bis(acryloxyneopentyl glycol) adipate, 1,3-butylene glycol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, propylene glycol diacrylate, polypropylene glycol diacrylate, 2-hydroxy-1,3-diacryloxy propane, 2,2-bis[4-(acryloxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxydiethoxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxypolyethoxy)-phenyl]propane, hydroxyl pivalic acid neopentyl glycol diacrylate, 1,4-butanediol diacrylate, dicyclopentanyl diacrylate, dipentaerythritol hexaacrylate, dipentaerythritol monohydroxypentaacrylate, ditrimethylolpropane tetraacrylate, pentaerythritol

triacrylate, tetrabromobisphenol A diacrylate, triglycerol diacrylate, trimethylolpropane triacrylate, tris(acryloxyethyl) isocyanurate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, propylene glycol dimethacrylate, polypropylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, 2-hydroxy-1,3-dimethacryloxypropane, 2,2-bis[4-(methacryloxy)phenyl]propane, 2,2-bis[4-(methacryloxyethoxy)-phenyl]propane, 2,2-bis[4-(methacryloxyethoxy diethoxy)-phenyl]propane, 2,2-bis[4-(methacryloxyethoxy polyethoxy)-phenyl]propane, tetrabromobisphenol A dimethacrylate, dicyclopentanyldimethacrylate, dipentaerythritol hexamethacrylate, glycerol dimethacrylate, hydroxyl pivalic acid neopentyl glycol dimethacrylate, dipentaerythritol monohydroxypentamethacrylate, ditrimethylolpropane tetramethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, triglycerol dimethacrylate, trimethylolpropane trimethacrylate, tris(methacryloxyethyl)isocyanurate, allyl methacrylate, divinylbenzene, diallyl phthalate, diallyl terephthalate, diallyl isophthalate and

diethylene glycol bisallylcarbonate.

The microencapsulated pigment of the invention having the crosslinked structure has a long-term excellent storage stability in the aqueous medium including various aqueous organic solvents and water and has a long-term excellent storage stability in the aqueous medium including a compound selected from the group consisting of glycol ethers and 1,2-alkylene glycol-based surfactants or a compound selected from the group consisting of acetylene glycol-based surfactants and acetylene alcohol-based surfactants. Although the reason for this is not clear, it is conceivable as one reason for this that the solvent resistance is improved due to the polymer having the crosslinked structure.

The added amount of the cross-linking monomer is preferably within the range of 0.0001 to 0.05 time the molarity of the above-mentioned hydrophobic monomer, and more preferably in the range of 0.001 to 0.01 time the molarity thereof. Exceeding 0.05 time the molarity of the hydrophobic monomer unfavorably results in the occurrence of a deterioration in fixability or abrasion resistance, and an increase in particle size in some cases. It is preferred that the amount of the above-mentioned crosslinking monomer added is appropriately decided within the above-mentioned range, considering the solvent

resistance, fixability and abrasion resistance.

[0070]

The polymerization reaction between the polymerizable surfactants or the polymerization reaction between the polymerizable surfactant and the comonomer can be started preferably by adding a polymerization initiator thereto, and particularly, a water-soluble polymerization initiator is preferably used as the polymerization initiator. Examples of the polymerizable initiator can include potassium persulfate, ammonium persulfate, sodium persulfate, 2,2-azobis-(2-methyl-propionamidine) dihydrochloride and 4,4-azobis-(4-cyano-valeric acid).

[0071]

In the invention, the wet pigment, the polymerizable surfactant, and aqueous medium are put into a reaction vessel equipped with a ultrasonic generator, a stirrer, a reflux condenser, a dropping funnel, and a temperature controller and an ultrasonic wave is irradiated thereto for a predetermined time. Then, the comonomer is added thereto as needed, followed by ultrasonication for a specified period of time elevate the system up to a predetermined polymerization temperature, and an aqueous solution of the water-soluble polymerization initiator in pure water is added dropwise to conduct a polymerization reaction while irradiating ultrasonic waves, thereby being

able to suitably obtain the microencapsulated pigment of the invention. After the termination of the polymerization, impurities such as unreacted materials are removed by centrifugal filtration and/or ultrafiltration, and the pH is preferably adjusted to the range of 7.0 to 9.0. Coarse particles are preferably removed by further filtration. The aqueous medium as used herein means a solvent containing water as a main component, and may contain a water-soluble organic solvent such as a glycerol or a glycol as an optional component, in addition to water. Further, the polymerization temperature is preferably within the range of 60 to 90°C.

[0072]

In the microencapsulate pigment of the invention obtained as described above, it is conceivable that the pigment particles are completely encapsulated with the polymer layer (without defects), and that the hydrophilic groups are regularly orientated toward the aqueous medium in the uppermost layer of the encapsulating polymer (see Fig. 2). Accordingly, the pigment has high dispersion stability to the aqueous medium.

[0073]

Although the microencapsulated pigment according to the embodiment of the invention is described above, the particle size of the microencapsulated pigment is

preferably 400 nm or less, more preferably 300 nm or less, and particularly preferably from 50 to 200 nm.

[0074]

[Aqueous Dispersion]

The aqueous dispersion according to an embodiment of the invention contains the microencapsulated pigment according to the embodiment of the invention, and as such an aqueous dispersion, there can be suitably exemplified the solution after emulsion polymerization described in the above-mentioned embodiment. Other compounding components for obtaining the ink for ink jet recording are further normally added to the aqueous dispersion, thereby being able to prepare the ink for ink jet recording according to an embodiment of the invention.

[0075]

[Ink for Ink Jet Recording]

As described above, the ink for ink jet recording according to the embodiment of the invention contains the aqueous dispersion.

Further, the ink for ink jet recording according to another embodiment of the invention contains at least the microencapsulated pigment according to the embodiment of the invention and water. The content of the microencapsulated pigment is preferably from 1 to 20% by weight, and more preferably from 3 to 15% by weight, based



on the total weight of the ink for ink jet recording. In particular, in order to obtain high print density and high color developability, it is preferably from 5 to 15% by weight.

[0076]

A solvent for the ink for ink jet recording according to the embodiment of the invention preferably contains water and a water-soluble organic solvent as basic solvents, and may contain other components as needed.

[0077]

Examples of the water-soluble organic solvents can include alkyl alcohols having 1 to 4 carbon atoms such as ethanol, methanol, butanol, propanol, and isopropanol, glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxy butanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl

ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, and dipropylene glycol mono-n-butyl ether, formamide, acetamide, dimethyl sulfoxide, sorbite, sorbitan, acentine, diacetine, triacetine, and sulforan.

[0078]

In order to impart water retentivity and wetting properties to the ink for ink jet recording, the ink for ink jet recording according to the embodiment of the invention preferably contains a wetting agent comprising a high boiling-point water-soluble organic solvent as a water-soluble organic solvent. Such a high boiling-point water-soluble organic solvent is a high boiling-point water-soluble organic solvent having a boiling point of 180°C or higher.

[0079]

Specific examples of the water-soluble organic solvents having a boiling point of 180°C or higher, which can be used in the invention, include ethylene glycol, propylene glycol, diethylene glycol, pentamethylene glycol, trimethylene glycol, 2-butene-1,4-diol, 2-ethyl-1,3-hexanediol, 2-methyl-2,4-pentanediol, tripropylene glycol

monomethyl ether, dipropylene glycol monoethyl glycol, tetraethylene glycol, triethylene glycol, tripropylene glycol, polyethylene glycol having a molecular weight of 2,000 or less, 1,3-propylene glycol, isopropylene glycol, isobutylene glycol, glycerol, meso-erythritol and pentaerythritol. It is more preferred that the high boiling water-soluble organic solvent used in the invention has a boiling point of 200°C or higher. One or two or more of them can be used in the ink of the invention. Addition of the high boiling water-soluble organic solvent to the ink can provide the ink for ink jet recording which retains flowability and re-dispersibility for a long period of time even when it is allowed to stand in an open state (a state in which the ink is in contact with air at room temperature). Further, such an ink is hard to clog ink jet nozzles during printing using an ink jet printer or on restarting after the interruption of printing, so that the ink having high ejection stability from the ink jet nozzles is obtained.

[0080]

The total content of the water-soluble organic solvent is preferably in the range of 10 to 50% by weight, and more preferably in the range of 10 to 30% by weight, based on the total weight of the ink for ink jet recording.

[0081]

Examples of the water-soluble organic solvent can include 2-pyrrolidone, N-methylpyrrolidone,  $\epsilon$ -caprolactam, dimethyl sulfoxide, sulforane, morpholine, N-ethylmorpholine and 1,3-dimethyl-2-imidazolidinone can be added to the ink and one or more thereof may be selected and used. Addition of the polar solvent can provide the effect of improving the dispersibility of the encapsulated pigment particles in the ink to improve the ejection stability of the ink.

The content of the polar solvent is preferably in the range of 0.1 to 20% by weight and more preferably in the range of 1 to 10% by weight, based on the total weight of the ink for ink jet recording.

[0082]

In order to accelerate penetration of the aqueous medium into the recording medium, it is preferred that the ink for ink jet recording according to an embodiment of the invention further contains a penetrant. Prompt penetration of the aqueous medium into the recording medium can provide recorded matter having images with less blurring. As such penetrants, there are preferably used an alkyl ether of a polyhydric alcohol (also referred to as a glycol ether) and a 1,2-alkyldiol. The alkyl ethers of polyhydric alcohols include, for example, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether,

ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-i-propyl ether, diethylene glycol mono-i-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-i-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-i-propyl ether, propylene glycol mono-n-butyl ether and dipropylene glycol mono-n-butyl ether. The 1,2-alkyldiols include, for example, 1,2-pentanediol and 1,2-hexanediol. Besides, the penetrants may selected from diols of straight-chain hydrocarbons such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol and 1,8-octanediol.

[0083]

In particular, in an embodiment of the invention, it is preferred that at least one selected from propylene glycol monobutyl ether, dipropylene glycol monobutyl ether,

diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, 1,2-pentanediol and 1,2-hexanediol is used as the penetrant. The total content of these penetrants is preferably from 1 to 20% by weight, and more preferably from 1 to 10% by weight, based on the total weight of the ink for ink jet recording. When the content of the penetrant is adjusted to 1% by weight or more, the effect of improving the penetrability of the ink into the recording medium is obtained. Further, adjustment to 20% by weight or less can prevent the occurrence of blurring in images printed using this ink, and can prevent an excessive increase in the viscosity of the ink. In particular, when the 1,2-alkyldiol such as 1,2-pentanediol or 1,2-hexanediol is used in the ink, drying properties of the ink after printing are improved, and blurring in images can be decreased.

[0084]

Particularly, in the embodiments of the invention, by allowing the ink to contain one or more selected from the group consisting of glycerol, alkyl ether of polyhydric alcohol, and 1,2-alkyl diol, it is possible to enhance penetrability of the ink solvent component into the recording medium while sufficiently securing clogging reliability and storage stability of the ink itself. Accordingly, in view of the effect of the

microencapsulated pigment according to the embodiment of the invention, it is possible to greatly reduce the blurring of an image in the process of performing a printing operation on the plain paper or a recycled paper and to enhance the print quality.

[0085]

When the above-mentioned glycol ethers are used, it is particularly preferable that glycol ethers are used along with an acetylene glycol compound as a surfactant to be described later.

[0086]

Furthermore, it is preferred that the ink for ink jet recording according to an embodiment of the invention contains a surfactant, particularly an anionic surfactant and/or a nonionic surfactant. Specific examples of the anionic surfactants include an alkanesulfonate, an  $\alpha$ -olefinsulfonate, an alkylbenzenesulfonate, an alkylnaphthalenesulfonic acid, an acylmethyltaurinic acid, a dialkylsulfosuccinic acid, an alkylsulfuric ester salt, a sulfated oil, a sulfated olefin, a polyoxyethylene alkyl ether sulfuric ester salt, a fatty acid salt, an alkylsarcosine salt, an alkylphosphoric ester salt, a polyoxyethylene alkyl ether phosphoric ester salt and a monoglyceride phosphoric ester salt. Further, specific examples of the nonionic surfactants include a

polyoxyethylene alkyl ether, a polyoxyethylene alkyl phenyl ether, a polyoxyethylene alkyl ester, a polyoxyethylene alkylamide, a glycerol alkyl ester, a sorbitan alkyl ester, a sugar alkyl ester, a polyhydric alcohol alkyl ether and an alkanolamine fatty acid amide.

[0087]

More specifically, the anionic surfactants include ether surfactants such as sodium dodecylbenzenesulfonate, sodium laurate and an ammonium salt of a polyoxyethylene alkyl ether sulfate. Specific examples of the nonionic surfactants include polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene dodecyl phenyl ether, a polyoxyethylene alkyl allyl ether, polyoxyethylene oleyl ether, polyoxyethylene lauryl ether, a polyoxyethylene alkyl ether and a polyoxyalkylene alkyl ether, and ester surfactants such as polyoxyethylene oleic acid, polyoxyethylene oleic acid ester, polyoxyethylene distearic acid ester, sorbitan laurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, polyoxyethylene monooleate and polyoxyethylene stearate.

[0088]

In particular, it is desirable that the ink for ink jet recording according to an embodiment of the invention contains an acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant. The aqueous medium

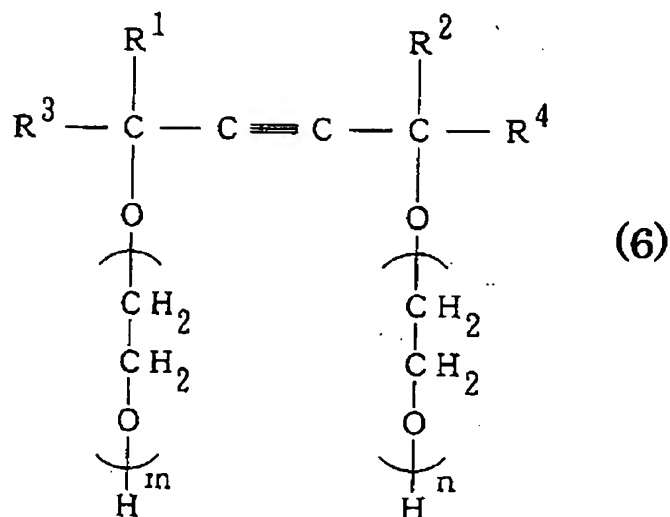


contained in the ink becomes easy to penetrate into the recording medium thereby, so that images having little blurring can be printed on various recording media.

Preferred specific examples of the acetylene glycol-based surfactants used in the invention include a compound represented by the following formula (6).

[0089]

[Kagaku 10]



wherein m and n are each a number satisfying  $0 \leq m+n \leq 50$ ; and  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are each independently an alkyl group (preferably, an alkyl group having 6 or less carbon atoms).

Of the compounds represented by the above formula (6), particularly preferred are 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol and 3,5-dimethyl-1-hexyne-3-ol. As the compounds represented by the above formula (6), it is also possible to utilize

commercial products commercially available as the acetylene glycol-based surfactants. Specific examples thereof include Surfynol 104, 82, 465, 485 and TG (all are available from Air Products and Chemicals, Inc.), and Olfine STG and Olfine E1010 (trade names, manufactured by Nissin Chemical Industry Co., Ltd.).

[0090]

The acetylene alcohol-based surfactants include Surfynol 61 (available from Air Products and Chemicals, Inc.).

[0091]

The content of the surfactant is in the range of 0.01 to 10% by weight and more preferably in the range of 0.1 to 5% by weight, based on the total weight of the ink for ink jet recording.

[0092]

Further, the ink for ink jet recording according to the embodiment of the invention can contain a pH adjuster. The pH of the ink is adjusted preferably to 7 to 9, and more preferably to 7.5 to 8.5.

Preferred specific examples of the pH adjusters include potassium metal compounds such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, sodium hydrogencarbonate, potassium carbonate, lithium carbonate, sodium phosphate, potassium phosphate, lithium

phosphate, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, sodium oxalate, potassium oxalate, lithium oxalate, sodium borate, sodium tetraborate, potassium hydrogenphthalate and potassium hydrogentartrate; ammonia; and amines such as methyl amine, ethylamine, diethylamine, trimethylamine, triethyl amine, tris(hydroxymethyl)aminomethane hydrochloride, triethanolamine, diethanolamine, diethylethanolamine, triisopropenol amine, butyldiethanolamine, morpholine and propanol amine.

Of these, when an alkali hydroxide compound or an amine alcohol added to the ink, the dispersion stability of the microencapsulated pigment particles of the invention in the ink can be improved.

The added amount of the alkali hydroxide compound is preferably in the range of 0.01 to 5% by weight, and more preferably in the range of 0.05 to 3% by weight, based on the total weight of the ink.

The added amount of the amine alcohol is preferably in the range of 0.1 to 10% by weight, and more preferably in the range of 0.5 to 5% by weight, based on the total weight of the ink.

[0093]

Further, for the purpose of mildewproofing, antiseptis or rust prevention, at least one compound

selected from benzoic acid, dichlorophene, hexachlorophene, sorbic acid, a p-hydroxybenzoic ester, ethylenediamine tetraacetic acid (EDTA), sodium dehydroacetate, 1,2-benthiazolin-3-on (product name: Proxel XL manufactured by Avecia) and 4,4-dimethyloxazolidine can be added to the ink for ink jet recording.

Furthermore, for the purpose of preventing nozzles of a recording head from being dried, at least one selected from the group consisting of urea, thiourea and ethylene urea can also be added to the ink for ink jet recording.

[0094]

A particularly preferred embodiment of the ink for ink jet recording of the invention is an ink containing at least

- (1) the above-mentioned microencapsulated pigment,
- (2) at least one compound (penetrant) selected from the group consisting of diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and an 1,2-alkyldiol having 4 to 10 carbon atoms,
- (3) glycerol, and
- (4) water.

Another particularly preferred embodiment of the ink for ink jet recording of the invention contains at least

(1) the microencapsulated pigment according to the embodiment of the invention,

(2) at least one compound (penetrant) selected from the group consisting of diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and an 1,2-alkyldiol having 4 to 10 carbon atoms,

(3) the acetylene glycol-based surfactant and/or the acetylene alcohol-based surfactant,

(4) glycerol, and

(5) water.

Such ink for ink jet recording particularly has excellent dispersion stability and ejection stability and does not have the clogging of the nozzles for a long period of time, thereby stably performing a printing operation. In the recording medium such as the plain paper, the recycled paper, and the coated paper, the drying property after the printing operation is excellent and the blurring is little, thereby obtaining a high-quality image with a high print density and excellent color developability.

[0095]

In general, the dispersant such as a surfactant or a polymer dispersant is used to disperse the pigment. Since the dispersants are simply adsorbed on the surfaces of the pigment particles, the dispersants tends to be separated

from the surfaces of the pigment particles due to some environmental reasons. On the contrary, in the embodiment of the invention, since the polymer coating or the crosslinking polymer coating surrounding the surfaces of the pigment surfaces completely including the surfaces of the pigment particles having a hydrophilic group with the polymer coating or the crosslinking polymer coating is secured very strongly to the surfaces of the pigment particles as described above, the dispersant is hardly separated from the surfaces of the pigment particles.

[0096]

More specifically, in the ink of which the penetrability has been improved with the acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant, and a penetrant such as diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, and 1,2-alkyl diol by the use of the pigment dispersion in which the pigment is dispersed using a surfactant or a dispersant such as a polymer dispersant, the dispersant is easily separated from the surfaces of the pigment particles due to the strong shearing force applied when the ink is ejected through a thin nozzle, thereby deteriorating the dispersibility and making the ejection unstable.

[0097]

On the contrary, in the ink for ink jet recording using the microencapsulated pigment according to the embodiment of the invention, such a phenomenon is not recognized to eject the ink stably. Since the pigment particles are encapsulated with the polymer coating or the crosslinking polymer coating to obtain excellent solvent resistance, the promotion of the separation from the pigment particles or the expansion of the polymer due to the penetrant hardly occurs, thereby maintaining the excellent dispersion stability for a long period of time.

[0098]

In the ink composition employing the pigment dispersion in which the pigment is dispersed using the dispersant such as the surfactant or the polymer dispersant and having improved penetrability, since the viscosity of the ink composition tends to increase due to the dispersant not adsorbed on the surfaces of the pigment particles but dissolved in the solution at the initial time of dispersion or there is a tendency that the dispersant separated from the pigment particles after being dispersed and the content of the pigment is often restricted. Accordingly, in the plain paper or the recycled paper, a sufficient print density cannot be obtained and thus excellent color developability cannot be

often obtained. On the contrary, in the ink composition using the microencapsulated pigment according to the embodiment of the invention, since the pigment particles are encapsulated with the polymer coating or the crosslinking polymer coating as described above, the dispersant is not easily separated from the pigment particles and thus the viscosity of the ink composition does not increase. Accordingly, it is easy to decrease the viscosity of the ink composition and it is possible to more contain the pigment particles, thereby obtaining a sufficient print density on the plain paper or the recycled paper.

[0099]

In the above-mentioned preferable embodiment of the invention, the added amount of the acetylene glycol-based surfactant and/or the acetylene alcohol-based surfactant in the (2) is preferably in the range of 0.01 to 10% by weight and more particularly in the range of 0.1 to 5% by weight, based on the total weight of the ink.

[0100]

In the particularly preferable embodiment of the invention, the added amount of diethylene glycol monobutyl ether and triethylene glycol monobutyl ether as the penetrant of (3) is preferably 10% by weight or less, and more preferably in the range of 0.5 to 5% by weight, based



on the total weight of the ink. Addition of diethylene glycol monobutyl ether and/or triethylene glycol monobutyl ether can improve penetrability of the ink. Further, the addition of diethylene glycol monobutyl ether and/or triethylene glycol monobutyl ether also have the effect of improving solubility of the acetylene glycol-based surfactant and print quality.

[0101]

In the particularly preferable embodiment of the invention, the amount added at the time when the 1,2-alkyldiol having 4 to 10 carbon atoms of (3) as the penetrant is added to the ink is 15% by weight or less based on the total weight of the ink. When the 1,2-alkyldiol having 3 or less carbon atoms is used, sufficient penetrability into the recording medium is not obtained. The 1,2-alkyldiol having 16 or more carbon atoms is unfavorable because it becomes difficult to dissolve in water. When the amount of the 1,2-alkyldiol in the ink exceeds 15% by weight, the viscosity of the ink unfavorably tends to increase. Specifically, 1,2-pentanediol or 1,2-hexanediol is preferably used as the 1,2-alkyldiol. Either one can be used alone, or both can be used in combination. 1,2-alkyldiol added to the ink is preferably in the range of 0.1 to 15% by weight. The added amount of 1,2-hexandiol is preferably in the range

of 0.5 to 10% by weight. When the added amount of 1,2-Hexanediol is smaller than 0.5 % by, good penetrability cannot be obtained.

[0102]

Further, when the ink of each embodiment described above is used in the ink jet recording process, in order to make it difficult to generate the clogging of the ink jet nozzles (improvement in clogging reliability), and in order to inhibit the occurrence of white blanks (fine places having no ink on the recording medium) in an image region of printed matter obtained by the ink jet recording process using the ink of each embodiment described above, a solid wetting agent is preferably added in an amount of 3 to 20% by weight based on the total weight of the ink.

The above-mentioned solid wetting agent means a water-soluble substance which is solid at ordinary temperature (25°C) and has a water-retaining function. Preferred examples of the solid wetting agents include a saccharide, a sugar alcohol, a hyaluronate, trimethylolpropane and 1,2,6-hexanetriol. Examples of the saccharides include a monosaccharide, a disaccharide, an oligosaccharide (including a trisaccharide and a tetrasaccharide) and a polysaccharide. Preferred examples thereof include glucose, mannose, fructose, ribose, xylose, arabinose, galactose, aldonic acid, glucitol, sorbit,

maltose, cellobiose, lactose, sucrose, trehalose and maltotriose. The term "polysaccharide" as used herein means a saccharide in its broad sense, and is used in the sense that it includes substances widely occurring in nature such as alginic acid,  $\alpha$ -cyclodextrin and cellulose. Further, derivatives of these saccharides include a reduced sugar of the above-mentioned saccharide (for example, a sugar alcohol represented by the general formula  $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$  (wherein  $n$  represents an integer of 2 to 5), an oxidized sugar (for example, an aldonic acid or a uronic acid), an amino acid and a thiosugar. In particular, a sugar alcohol is preferred, and specific examples thereof include maltitol, sorbitol and xylitol. As the hyaluronate, there can be used a product commercially available as a 1% aqueous solution of sodium hyaluronate (molecular weight: 350,000). The solid wetting agents may be used alone or as a mixture of two or more.

[0103]

The use of the solid wetting agent can restrain the evaporation of water by its water retaining function, so that the viscosity of the ink does not increase in flow paths of the ink or in the vicinities of ink jet nozzles, and the film formation caused by the evaporation of water of the ink also becomes difficult to occur, which causes

difficulty in clogging the nozzles. Further, the above-mentioned solid wetting agent is chemically stable, so that it does not decompose in the ink, and the quality of the ink can be maintained for a long period of time. Furthermore, even when the above-mentioned solid wetting agent is added to the ink, the ink does not wet a nozzle plate, and can be stably ejected from the ink jet nozzles.

[0104]

In the invention, when the above-mentioned solid wetting agents are used alone, the content thereof is preferably from 3 to 20% by weight, and more preferably from 3 to 10% by weight, based on the total weight of the ink. When two or more thereof are used as a mixture, the total amount of two or more thereof is preferably from 3 to 20% by weight, and more preferably from 3 to 10% by weight, based on the total weight of the ink for ink jet recording. When two or more thereof are used as a mixture, preferred is a combination of one selected from the group consisting of a saccharide, a sugar alcohol and a hyaluronate and one selected from the group consisting of trimethylolpropane and 1,2,6-hexanetriol. This combination is preferred because an increase in the viscosity of the ink by addition can be restrained. When the content of the solid wetting agents is less than 3% by weight, the sufficient effect of improving the clogging is

not obtained. On the other hand, exceeding 20% by weight results in the tendency of the harmful effect to occur that the viscosity increases to become hard to obtain stable ejection.

[0105]

Although the ink for ink jet recording according to the embodiment of the invention has been described above, the microencapsulated pigment according to the embodiment of the invention contained as the colorant is small in the particle size of the colorant particles, and shaped like a true sphere. Accordingly, flowability of the ink easily becomes Newtonian. Further, the hydrophilic groups on the surface are regularly densely orientated toward the aqueous medium side, so that electrostatic repulsion is considered to be effectively generated. There can be therefore prepared the ink for ink jet recording which is excellent in ejection stability, more excellent in dispersibility (high dispersibility) and dispersion stability and further improved in the concentration of the colorant contained, compared to the conventional microencapsulated pigments.

[0106]

The ink jet recording can be suitably achieved by mounting the ink for ink jet recording according to the embodiment of the invention on a known ink jet printer,

and printing the ink on the recording medium such as plain paper or an ink jet recording medium. This allows ejection stability of the ink from a recording head to be excellent, and can provide the recorded matter which is excellent in fastness, abrasion resistance, and color developability of images, and high in image density of images, and in which images are hard to blur. Further, even when plain paper is used as the recording medium, the recorded matter is obtained in which images are hard to blur, and which is excellent in color developability of images.

[0107]

[Examples]

Hereinafter, the invention will be more specifically described with reference to examples and comparative examples, but the invention is not limited to the examples.

[0108]

#### Preparation of Microencapsulated Pigment "MCP1"

A hundred grams of a wet cyan pigment (C.I. Pigment Blue 15:3 having a water content of 60%), 10 g of a polymerizable surfactant, Aqualon KH-10, and 50 g of ion exchanged water were added and mixed, and then, dispersed in an Eiger Motor Mill, Model 250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 1 hour. This was put into a

reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. Then, after the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, a 5-fold excess of isopropyl alcohol was added to precipitate a polymerization product, and the polymerization product was further sedimented with a centrifugal separator to remove a supernatant. Then, 250 g of ion exchanged water was added thereto, followed by irradiation with an ultrasonic wave of 45 KHz for 30 minutes to disperse the product again. The resulting dispersion was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP1".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leads & Northlop Co. As a result, it was about 300 nm.

[0109]

#### Preparation of Microencapsulated Pigment "MCP2"

A hundred grams of a wet magenta pigment (C.I. Pigment Red 122 having a water content of 60%), 10 g of a polymerizable surfactant, Aqualon KH-10, 12 g of benzyl methacrylate, 8 g of dodecyl methacrylate and 50 g of ion exchanged water were added and mixed, followed by dispersion treatment in a Microfluidizer M-140K (manufactured by Microfluidics Corporation) for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. Then, after the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, a 5-fold excess of isopropyl alcohol was added to precipitate a polymerization product, and the polymerization product was further sedimented with a centrifugal separator to remove a supernatant. Then, 250 g of ion exchanged water was added thereto, followed by irradiation with an ultrasonic wave of 45 KHz for 30



minutes to disperse the product again. The resulting dispersion was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1  $\mu$ m to remove coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP2".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 300 nm.

[0110]

#### Preparation of Microencapsulated Pigment "MCP3"

A hundred grams of a wet yellow pigment (C.I. Pigment Yellow 17 having a water content of 60%), 15 g of a polymerizable surfactant, Adeka Reasoap SE-10N, 5 g of isobornyl methacrylate, 8 g of dodecyl methacrylate, 0.5 g of 2-acrylamido-2-methylpropanesulfonic acid and 50 g of ion exchanged water were added and mixed, and then, dispersed in an Eiger Motor Mill, Model 250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. After the internal temperature of the reaction

vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, the resulting product was filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove coarse particles, and then, subjected to ultrafiltration. Then, 150 g of ion exchanged water was added thereto, followed by irradiation with an ultrasonic wave of 45 KHz for 30 minutes to disperse the product. The resulting dispersion was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP3".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 300 nm.

[0111]

#### Preparation of Microencapsulated Pigment "MCP4"

A hundred grams of a wet cyan pigment (C.I. Pigment Blue 15:4 having a water content of 60%), 15 g of a

polymerizable surfactant, Aqualon KH-10, 7 g of benzyl methacrylate, 4 g of dodecyl methacrylate, 0.1 g of diethylene glycol dimethacrylate, 0.5 g of 2-acrylamido-2-methylpropanesulfonic acid and 50 g of ion exchanged water were added and mixed, followed by dispersion treatment in a Microfluidizer M-140K (manufactured by Microfluidics Corporation) for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen--introducing pipe and an ultrasonic generator. After the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, the resulting product was filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove coarse particles, and then, subjected to ultrafiltration. Then, 150 g of ion exchanged water was added thereto, followed by irradiation with an ultrasonic wave of 45 KHz for 30 minutes to disperse the product. The resulting dispersion was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1

µm to remove coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP4".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 280 nm.

[0112]

#### Preparation of Microencapsulated Pigment "MCP5"

2-Methoxybenzamino-5-N,N'-diethylaminosulfonyl chloride (25.8 g) was normally diazotized to obtain a diazonium salt. This was mixed and coupled with a ground normally prepared from 38 g of 2-hydroxynaphthalene-3-carboxyl-5'-chloro-2',4'-dimethoxyanilide to obtain a slurry of C.I. Pigment Red 5. To 20 g of this slurry, 10 g of Aqualon KH-10 and 100 g of ion exchanged water were added and mixed, followed by dispersion treatment in a Microfluidizer M-140K (manufactured by Microfluidics Corporation) for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. After the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and

polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, a 5-fold excess of isopropyl alcohol was added to precipitate a polymerization product, and the polymerization product was further sedimented with a centrifugal separator to remove a supernatant. Then, 40 g of ion exchanged water was added thereto, followed by irradiation with an ultrasonic wave of 45 KHz for 30 minutes to disperse the product again. This was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1  $\mu$ m to remove coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP5".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 280 nm.

[0113]

#### Preparation of Microencapsulated Pigment "MCP6"

3,3'-Dichlorobenzine (17.4 g) was normally tetrazotized to obtain a tetrazonium salt. On the other hand, 29.5 g of acetoacet-meta-xylidide and 0.4 g of acetoacetanilide parasulfonic acid were dissolved by mixing in the presence of an alkali to prepare a ground by

a conventional method. Both solutions were mixed and coupled with each other to form a suspension of a pigment. To 20 g of this suspension, 5 g of a polymerizable surfactant, Adeka Reasoap SE-10N, 2 g of benzyl methacrylate, 3.14 g of n-butyl methacrylate and 50 g of ion exchanged water were added and mixed, and then, dispersed in an Eiger Motor Mill, Model 250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. After the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, the resulting product was filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove coarse particles, and then, subjected to ultrafiltration. Then, the resulting dispersion was adjusted to pH 9 with a 2 mol/l aqueous solution of potassium hydroxide, and filtered through a membrane filter having a pore size of 1  $\mu\text{m}$  to remove

coarse particles, thus obtaining a dispersion of desired microencapsulated pigment "MCP6".

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 280 nm.

[0114]

The results of measurements of the aspect ratio and the Zingg index of microencapsulated pigments "MCP1" to "MCP6" are shown in Table 1.

[0115]

[Table 1]

Microencapsulated Pigment	MCP1	MCP2	MCP3	MCP4	MCP5	MCP6
Aspect Ratio	1.0	1.0	1.0	1.0	1.0	1.0
Zingg Index	1.0	1.0	1.0	1.0	1.0	1.0

[0116]

Preparation of Microencapsulated Pigments "MCP7" to "MCP10"

MCP7 (microencapsulated cyan pigment), MCP8 (microencapsulated cyan pigment), MCP9 (microencapsulated magenta pigment) and MCP10 (microencapsulated yellow pigment) were produced based on a method described in Japanese Unexamined Patent Application Publication No. 10-

140065.

[0117]

#### Preparation of "MCP7"

A flask was charged with 250 g of methyl ethyl ketone, the temperature of which was elevated to 75°C with stirring under a nitrogen seal. A mixed solution of 85 g of n-butyl methacrylate, 90 g of n-butyl acrylate, 40 g of 2-hydroxyethyl methacrylate, 25 g of methacrylic acid and 20 g of a polymerization initiator, Perbutyl O (tert-butyl peroxyoctoate manufactured by Nippon Oil & Fats Co., Ltd.) was added dropwise thereto for 2 hours, followed by further reaction for 15 hours to obtain a solution of a vinyl polymer.

Into a stainless steel beaker, 8 g of the above-mentioned polymer solution was put together with 0.4 g of dimethylethanolamine and 8 g of a cyan pigment (C.I. Pigment Blue 15:3), and ion exchanged water was further added to bring the total amount to 40 g. Then, 250 g of zirconia beads having an average particle size of 0.5 mm was added thereto, followed by kneading with a sand mill for 4 hours. After the termination of the kneading, the zirconia beads were removed by filtration to obtain an aqueous dispersion in which a dispersion comprising the polymer having the carboxyl group neutralized with the base and the pigment was dispersed in water. A 1 N



hydrochloric acid was added to the resulting dispersion with stirring with a dispersing device at ordinary temperature until the resin was insolubilized to be firmly fixed to the pigment. At this time, the pH was 3 to 5. The aqueous medium containing the pigment to which the polymer was firmly fixed was filtered by suction and washed with water to obtain a wet cake. A 10% aqueous solution of NaOH added thereto, while stirring the wet cake with a dispersing device, until the pH of the dispersion reached 8.5 to 9.5, and stirring was continued for 1 hour. Then, ion exchanged water was added to adjust the solid concentration to 20%, thereby obtaining microencapsulated pigment MCP7 of carbon black. The aspect ratio thereof was 1.4, and the Zingg index thereof was 1.4.

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 180 nm.

[0118]

#### Preparation of "MCP8"

A flask was charged with 250 g of methyl ethyl ketone, the temperature of which was elevated to 75°C with stirring under a nitrogen seal. A mixed solution of 155 g of n-butyl methacrylate, 20 g of n-butyl acrylate, 35 g of

2-hydroxyethyl methacrylate, 40 g of methacrylic acid and 5 g of a polymerization initiator, Perbutyl O, was added dropwise thereto for 2 hours, followed by further reaction for 15 hours to obtain a solution of a vinyl polymer.

Into a stainless steel beaker, 10 g of the above-mentioned polymer solution, 7 g of a cyan pigment (C.I. Pigment Blue 15:3), 40 g of methyl ethyl ketone and 150 g of ceramic beads having an average particle size of 0.5 mm were put, and dispersed with a beads mill dispersing device. Thereafter, the ceramic beads were removed by filtration to prepare a paste for a microencapsulated pigment.

Then, 20 g of the above-mentioned paste for a microencapsulated pigment was mixed with 0.2 g of diethanolamine to form an organic solvent phase, and 25 g of ion exchanged water was added dropwise for 20 minutes to the organic solvent phase with stirring while irradiating an ultrasonic wave to cause phase reversal of emulsion, thereby obtaining a microencapsulated pigment-containing aqueous dispersion.

Further, the microencapsulated pigment-containing aqueous dispersion was further distilled at 85°C, thereby removing the solvent. Thus, microencapsulated pigment MCP8 of C.I. Pigment Blue 15:3 was obtained. The aspect ratio thereof was 1.4, and the Zingg index thereof was 1.4.

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 180 nm.

[0119]

#### Production of "MCP9"

A flask was charged with 250 g of methyl ethyl ketone, the temperature of which was elevated to 75°C with stirring under a nitrogen seal. A mixed solution of 170 g of n-butyl methacrylate, 58 g of n-butyl acrylate, 35 g of 2-hydroxyethyl methacrylate, 35 g of acrylic acid and 20 g of a polymerization initiator, Perbutyl O, was added dropwise thereto for 2 hours, followed by further reaction for 15 hours to obtain a solution of a vinyl polymer.

Into a stainless steel beaker, 15 g of the above-mentioned polymer solution was put together with 0.8 g of dimethylethanolamine and 15 g of a magenta pigment (C.I. Pigment Red 122), and ion exchanged water was further added to bring the total amount to 75 g. Then, 250 g of zirconia beads having an average particle size of 0.5 mm was added thereto, followed by kneading with a sand mill for 4 hours. After the termination of the kneading, the zirconia beads were removed by filtration to obtain an aqueous dispersion in which a dispersion comprising the polymer having the carboxyl group neutralized with the

base and the pigment was dispersed in water. A 1 N hydrochloric acid was added to the resulting dispersion with stirring with a dispersing device at ordinary temperature until the resin was insolubilized to be firmly fixed to the pigment. At this time, the pH was 3 to 5. The aqueous medium containing the pigment to which the polymer was firmly fixed was filtered by suction and washed with water to obtain a wet cake. A 10% aqueous solution of NaOH added thereto, while stirring the wet cake with a dispersing device, until the pH of the dispersion reached 8.5 to 9.5, and stirring was continued for 1 hour. Then, ion exchanged water was added to adjust the solid concentration to 20%, thereby obtaining microencapsulated pigment MCP9 of C.I. Pigment Red 122. The aspect ratio thereof was 1.4, and the Zingg index thereof was 1.4.

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 250 nm.

[0120]

#### Production of "MCP10"

A flask was charged with 250 g of methyl ethyl ketone, the temperature of which was elevated to 75°C with stirring under a nitrogen seal. A mixed solution of 170 g

of n-butyl methacrylate, 5 g of n-butyl acrylate, 35 g of 2-hydroxyethyl methacrylate, 35 g of acrylic acid and 20 g of a polymerization initiator, Perbutyl O, was added dropwise thereto for 2 hours, followed by further reaction for 15 hours to obtain a solution of a vinyl polymer.

Into a stainless steel beaker, 15 g of the above-mentioned polymer solution was put together with 0.8 g of dimethylethanolamine and 15 g of a yellow pigment (C.I. Pigment Yellow 110), and ion exchanged water was further added to bring the total amount to 75 g. Then, 250 g of zirconia beads having an average particle size of 0.5 mm was added thereto, followed by kneading with a sand mill for 4 hours. After the termination of the kneading, the zirconia beads were removed by filtration to obtain an aqueous dispersion in which a dispersion comprising the polymer having the carboxyl group neutralized with the base and the pigment was dispersed in water. A 1 N hydrochloric acid was added to the resulting dispersion with stirring with a dispersing device at ordinary temperature until the resin was insolubilized to be firmly fixed to the pigment. At this time, the pH was 3 to 5. The aqueous medium containing the pigment to which the polymer was firmly fixed was filtered by suction and washed with water to obtain a wet cake. A 10% aqueous solution of NaOH added thereto, while stirring the wet

cake with a dispersing device, until the pH of the dispersion reached 8.5 to 9.5, and stirring was continued for 1 hour. Then, ion exchanged water was added to adjust the solid concentration to 20%, thereby obtaining microencapsulated pigment MCP10 of C.I. Pigment Yellow 110. The aspect ratio thereof was 1.4, and the Zingg index thereof was 1.4.

The number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 180 nm.

[0121]

#### Preparation of "MCP11"

Forty grams of a commercially available magenta pigment (C.I. Pigment Red 122, HOSTAPERM PINK EB TRANS manufactured by Clariant), 8 g of a polymerizable surfactant, Aqualon KH-10, 5 g of benzyl methacrylate, 8 g of dodecyl methacrylate and 200 g of ion exchanged water were added and mixed, followed by irradiation with an ultrasonic wave of 45 KHz for 1 hour. This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe and an ultrasonic generator. Then, after the internal temperature of the reaction vessel was elevated to 80°C, an aqueous solution of 0.2 g

of potassium persulfate, a polymerization initiator, dissolved in 10 g of ion exchanged water was added dropwise, and polymerization was conducted at 80°C for 3 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, the number average particle size was measured with a laser doppler system size distribution analyzer, Microtrac UPA150, manufactured by Leeds & Northrop Co. As a result, it was about 7  $\mu\text{m}$ .

[0122]

As described above, microencapsulated pigments "MCP1" to "MCP6" of Examples had a particle size of 300 nm or less, and further, "MCP20" and "MCP21" had a particle size of 150 nm or less. They had an aspect ratio of 1.0 and a Zingg index of 1.0 to show a true sphere shape. In contrast, microencapsulated pigments "MCP7" to "MCP11" of Comparative Examples had a particle size of 160 nm or more, and "MCP7" to "MCP10" had an aspect ratio of larger than 1.3 and a Zingg index of larger than 1.3 to show no true sphere shape. The aspect ratio and the Zingg index were determined by diluting the aqueous dispersion 100 times with ion exchanged water, drying it, observing the particles under a transmission electron microscope (TEM) and a scanning electron microscope (SEM), and measuring the major and minor diameters and thickness of the

particles.

[0123]

Then, surface-treated organic pigments "P1" to "P5" (corresponding to conventional example 1) were produced.

The "amount of hydrophilic groups introduced onto surfaces of pigment particles" shown below was determined by the following methods.

Determination of Amount of Hydrophilic Groups  
(Anionic Groups) Introduced

(When hydrophilic groups were introduced with a sulfonating agent)

Pigment particles whose surfaces are treated with a sulfonating agent were treated by an oxygen flask combustion method, and a 0.3% aqueous solution of hydrogen peroxide was absorbed by the pigment particles. Then, the sulfuric ion (bivalent) was determined by ion chromatography (Dionex Corporation; 2000i). The resulting value was converted to the value of the sulfonic acid group, and indicated as the equivalent per g of pigment.

(When hydrophilic groups were introduced with a carboxylating agent)

As a technique, the Zeisel method was used. Diazomethane was dissolved in an appropriate solvent, and the resulting solution was added dropwise to convert all active hydrogen atoms on the surfaces of the pigment



particles to methyl groups. Hydroiodic acid having a specific gravity of 1.7 was added to the pigment thus treated, followed by heating to vaporize the methyl groups as methyl iodide. The gas of methyl iodide was trapped with a silver nitrate solution to precipitate as methylsilver iodide. The amount of the original methyl groups, that is, the amount of active hydrogens, was measured from the weight of the silver iodide, and indicated as the molar quantity per g of pigment (mmol/g).

[0124]

#### Preparation of Black Pigment Particles "P1" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

Carbon black ("MA-7" manufactured by Mitsubishi Chemical Corporation) (15 parts) was mixed with 200 parts of sulfolane (a sulfonating agent), and dispersed in an Eiger Motor Mill, M250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 1 hour. A mixed solution of a pigment paste dispersed and a solvent was transferred to an evaporator, and heated at 120°C while reducing the pressure to 30 mmHg or lower, thereby removing water contained in the system by distillation as much as possible. Thereafter, the temperature was controlled to 150°C, and then, 25 parts of sulfur trioxide was added, and allowed to react for 6 hours. After the termination

of the reaction, the reaction product was washed several times with excess sulfolane, poured into water, and filtered, thereby obtaining black pigment particles "P1".

The amount of the hydrophilic groups (anionic groups) introduced into the resulting black pigment particles "P1" was 0.12 mmol per g of pigment.

[0125]

#### Preparation of Black Pigment Particles "P2" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

After commercially available acidic carbon black ("MA-100" manufactured by Mitsubishi Chemical Corporation) (300 g) was thoroughly mixed with 1,000 ml of water, 450 g of sodium hypochlorite (effective chlorine concentration: 12%) was added dropwise thereto, followed by stirring at 80°C for 15 hours. The resulting slurry was washed repeatedly with ion exchanged water while filtering it through Toyo filter paper No. 2. As a measure of the completion of washing, the slurry was washed until white turbidity became disappeared when a 0.1 N aqueous solution of silver nitrate was added to the ion exchanged water that passed through the filter. This pigment slurry was dispersed again in 2,500 ml of water, and desalted through a reverse osmosis membrane until the electric conductance reached 0.2 microsiemens or less. Further, the slurry was concentrated so as to give a pigment concentration of

about 15% by weight.

The resulting surface-treated pigment dispersion was acid treated (acidified with aqueous hydrochloric acid), concentrated, dried and finely pulverized to obtain a powder. As for this surface-treated carbon black powder, the surface-active hydrogen content was measured by the above-mentioned method. As a result, it was 2.8 mmol/g.

[0126]

#### Preparation of Cyan Pigment Particles "P3" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

A phthalocyanine pigment (C.I. Pigment Blue 15:3) (20 parts) was mixed with 500 parts of quinoline, and dispersed in an Eiger Motor Mill, M250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 2 hours. A mixed solution of a pigment paste dispersed and a solvent was transferred to an evaporator, and heated at 120°C while reducing the pressure to 30 mmHg or lower, thereby removing water contained in the system by distillation as much as possible. Thereafter, the temperature was controlled to 150°C, and then, 20 parts of a sulfonated pyridine complex (a sulfonating agent) was added, and allowed to react for 8 hours. After the termination of the reaction, the reaction product was washed several times with excess quinoline, poured into water, and

filtered, thereby obtaining cyan pigment particles "P3" having hydrophilic groups (anionic groups) on their surfaces.

The amount of the hydrophilic groups (anionic groups) introduced into the resulting cyan pigment particles "P3" was 0.04 mmol/g.

[0127]

Preparation of Yellow Pigment Particles "P4" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

Yellow pigment particles "P4" having the hydrophilic groups (anionic groups) on their surfaces were obtained by the same treating method as with the above-mentioned "preparation of cyan pigment particles "P3" having the hydrophilic groups on their surfaces" with the exception that "20 parts of the phthalocyanine pigment (C.I. Pigment Blue 15:3)" was substituted by "20 parts of an isoindolinone pigment (C.I. Pigment Yellow 110).

The amount of the hydrophilic groups (anionic groups) introduced into the resulting yellow pigment particles "P4" was 0.045 mmol/g.

[0128]

Preparation of Magenta Pigment Particles "P5" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

Magenta pigment particles "P5" having the hydrophilic groups (anionic groups) on their surfaces were

obtained by the same treating method as with the above-mentioned "preparation of cyan pigment particles "P3" having the hydrophilic groups on their surfaces" with the exception that "20 parts of the phthalocyanine pigment (C.I. Pigment Blue 15:3)" was substituted by "20 parts of an isoindolinone pigment (C.I. Pigment Red 122)".

The amount of the hydrophilic groups (anionic groups) introduced into the resulting yellow pigment particles "P5" was 0.06 mmol/g.

[0129]

Preparation of Inks for Ink Jet Recording

<Examples 1 to 8>

Inks for ink jet recording of Examples 1 to 8 were prepared, based on compositions shown in Table 2.

[0130]

[Table 2]

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Microencapsulated Pigment	MCP1	8	8					
	MCP2			8				
	MCP3				8			
	MCP4					8		
	MCP5						8	
	MCP6							8
Wetting Agent	Glycerol	15	13	12	13	13	13	13
Penetrant	Diethylene glycol monobutyl ether		5	3		5	5	
	Triethylene glycol monobutyl ether				2	5		2
	1,2-Hexanediol			2	2	3	3	2
	Trimethylolpropane		5	7	5	5	5	7
Solid Wetting Agent	1,2,6-Hexanetriol			5				
	Xylitol	1				0.5		
Polar Solvent	2-Pyrrolidone							
Surfactant	Olfine E1010			1		1		
pH Adjuster	Potassium hydroxide	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Preservative	Proxel XL-2	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Water	Ion exchanged water	bal.	bal.	bal.	bal.	bal.	bal.	bal.

The amounts added are all indicated by % by weight.

The amounts of the microencapsulated pigments are indicated by the solid concentration.

Inks for ink jet recording of Comparative Examples 1 to 26 were prepared, based on the compositions shown in Tables 3 to 6.

[0131]

<Comparative Examples 1 to 26>

[0132]

[Table 3]

## Ink Compositions of Inks for Ink Jet Recording of Comparative Examples

The amounts added are all indicated by % by weight.

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Microencapsulated Pigment	4	2	2	2	8	4	8	6
MCP7								
MCP8								
MCP9								
MCP10								
Wetting Agent	15	15	12	12	15	10	10	15
Glycerol						5	5	
Diethylene glycol								
Penetrant	6	6		6	7.5		6	6
Diethylene glycol monobutyl ether								
1,2-Hexanediol			6			7.5		
Surfactant	1	0.5	1	0.5	1	1	1	1
Surfynol 465					0.5	0.5		
Polyoxyethylene nonyl phenyl ether								
pH Adjuster								0.1
Potassium-hydroxide								
Propanolamine	2	3	3	3	3	3	3	
Preservative	0.05	0.05	1	1	0.05	1	0.05	1
Proxel XL 4,4-Dimethyloxazolidine								
Water	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.



[0133]

[Table 4]

Ink Compositions of Inks for Ink Jet Recording of Comparative Examples

		Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12	Comparative Example 13
Pigment	P1	6				
	P2		4			
	P3			6		
	P4				10	
	P5					8
Wetting Agent	Glycerol	15	10	10	12	15
	Diethylene glycol		2	2		
Penetrant	Diethylene glycol monobutyl ether	6	3		7.5	
	1,2-Hexanediol		3	6		7.5
	Surfynol 465	1	1	1	1	1
Surfactant	Polyoxyethylene nonyl phenyl ether			0.5	0.5	
	Potassium hydroxide	0.5	0.5			
pH Adjuster	Propanolamine			1	1	1
	Proxel XL	0.05	0.05			0.05
Preservative	4,4-Dimethyloxazolidine			1	1	
	Ion exchanged water	bal.	bal.	bal.	bal.	bal.

The amounts added are all indicated by % by weight.

The amounts of the microencapsulated pigments are indicated by the solid concentration.

[0134]

[Table 5]

Ink Compositions of Inks for Ink Jet Recording of Comparative Examples

Pigment	Comparative Example 14	Comparative Example 15	Comparative Example 16	Comparative Example 17	Comparative Example 18
Carbon Black	8	6			
C.I. Pigment Red 122			6		
C.I. Pigment Blue 15:3				6	
C.I. Pigment Yellow 185					6
Ammonium Salt of Styrene-Acrylic Acid Copolymer (molecular weight: 70,000, polymer composition: 38%)	1	1	1	1	1
Glycerol	15	10	10	15	10
Diethylene glycol	10	8	8	10	8
1,2-Hexanediol					5
2-Pyrrolidone		2	2		2
Olfine E1010		1	1		
Potassium hydroxide	0.1	0.1	0.1	0.1	0.1
Proxel XL-2	0.05	0.05	0.05	0.05	0.05
Ion exchanged water	bal.	bal.	bal.	bal.	bal.

The amounts added are all indicated by % by weight.

The amounts of the microencapsulated pigments are indicated by the solid concentration.

[0135]

[Table 6]

Ink Compositions of Inks for Ink Jet Recording of Comparative Examples

	Comp. Ex. 19	Comp. Ex. 20	Comp. Ex. 21	Comp. Ex. 22	Comp. Ex. 23	Comp. Ex. 24	Comp. Ex. 25	Comp. Ex. 26
Microencapsulated Pigment	MCP7	4			8			
	MCP8					8		
	MCP9		3				8	
	MCP10			3				8
Glycerol	15	15	15	15	15	10	10	15
Diethylene glycol						5	5	
Trimethylolpropane						6	6	6
Diethylene glycol monobutyl ether					8			
Triethylene glycol monobutyl ether								
1,3-Dimethyl-2- imidazolidinone			2	2				
2-Pyrrolidone	2	2						
Olfine E1010								
Surfynol 465	1	1	1	1	1	1	1	1
Potassium hydroxide	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Proxel XL-2	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Ion exchanged water	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.

[0136]

The inks for ink jet recording of Examples 1 to 8, Comparative Examples 1 to 26 and recorded matter printed using these inks were evaluated by methods shown below.

[0137]

#### Evaluation 1-1: Dispersibility 1

For each of the inks for ink jet recording of Examples and Comparative Examples, the storage modulus (Pa) at each angular speed at the time when the angular speed was applied from 0.5 rad/sec to 5 rad/sec was measured at 20°C with a PHYSICA MCR300 rheometer manufactured by Paar Physica using a cone plate (CP 75-1 manufactured by Paar Physica) having a cone radius of 37.50 mm, a cone angle of 1 degree, and a measuring gap of 0.05 mm. The storage modulus at 0.6 rad/sec was taken as  $G'_{\omega=0.6}$ , and the storage modulus at 0.8 rad/sec was taken as  $G'_{\omega=0.8}$ . The dispersibility of the ink was evaluated according to the following criteria.

[0138]

A: The value of  $(\log G'_{\omega=0.8} - \log G'_{\omega=0.6}) / (\log 0.8 - \log 0.6)$  is from 1.8 to 2.0.

B: The value of  $(\log G'_{\omega=0.8} - \log G'_{\omega=0.6}) / (\log 0.8 - \log 0.6)$  is from 1.6 to 1.8.

C: The value of  $(\log G'_{\omega=0.8} - \log G'_{\omega=0.6}) / (\log 0.8 - \log 0.6)$  is from 1.2 to 1.6.

D: The value of  $(\log G'_{\omega=0.8} - \log G'_{\omega=0.6}) / (\log 0.8 - \log 0.6)$  is less than 1.2.

[0139]

#### Evaluation 1-2: Dispersibility 2

For each of the inks for ink jet recording of Examples and Comparative Examples, the viscosity at angles of inclination of 70°, 60°, 50°, 40° and 30° was measured with an AMVn rolling ball viscometer at 20°C, using a capillary having an inner diameter of 0.9 mm and a steel ball having a diameter of 0.794 mm and a density of 7.850 g/cm<sup>3</sup>. The  $\sin \theta$  was plotted as abscissa and the viscosity as ordinate. The slope of the resulting  $\sin \theta$ -viscosity curve was determined, and the dispersibility of the ink was evaluated according to the following criteria.

[0140]

A: The slope of the  $\sin \theta$ -viscosity curve is from 0 to -0.05, and the ink indicates Newtonian properties and shows particularly good dispersibility.

B: The slope of the  $\sin \theta$ -viscosity curve is from -0.05 to -0.1, and the ink indicates nearly Newtonian properties and shows good dispersibility next to that of A.

C: The slope of the  $\sin \theta$ -viscosity curve is from -0.1 to -0.15, and the ink indicates non-Newtonian properties, but shows slightly good dispersibility.

D: The slope of the  $\sin \theta$ -viscosity curve is less

than -0.15, and the ink indicates non-Newtonian properties. Sedimentation easily occurs to show poor dispersibility.

[0141]

#### Evaluation 2: Dispersion Stability

Each of the inks for ink jet recording of Examples and Comparative Examples was put into a glass sample bottle, sealed, and then, allowed to stand at 60°C for 2 weeks. The viscosity of the ink before and after the standing was examined. The viscosity at a shear rate of 150/S was measured was measured at 20°C with a PHYSICA MCR300 rheometer manufactured by Paar Physica using a cone plate (CP 75-1 manufactured by Paar Physica) having a cone radius of 37.50 mm, a cone angle of 1° and a measuring gap of 0.05 mm. The results thus obtained were evaluated according to the following criteria.

A: The change is less than  $\pm 0.1$  mPa·s.

B: The change is from  $\pm 0.1$  to  $\pm 0.3$  mPa·s.

C: The change is  $\pm 0.3$  mPa·s or more.

[0142]

#### Evaluation 3: Sedimentation Properties

For each of the inks for ink jet recording of Examples and Comparative Examples, the sedimentation properties of the colorant in the ink were measured at 20°C using a TURBISCAN 2000 instrument (manufactured by FORMUL ACTION) which can evaluate the sedimentation

properties from intensity distributions of back scattered light and transmitted light in the height direction of the sample. A measurement principle of the TURBISCAN 2000 instrument manufactured by FORMUL ACTION is shown below. This instrument has the mechanism that when a glass tube into which an ink is put is set to a specified position of the instrument and a measurement is started, a stage disposed so as to surround the periphery (diameter direction) of the glass tube moves up and down along the glass tube. A light source and detectors for scattered light and transmitted light installed on the stage measure the intensity distributions of scattered light and transmitted light at 40- $\mu$ m intervals in the longitudinal direction of the glass tube, in response to the vertical movement of the stage. This operation is repeated at arbitrary time intervals, thereby being able to observe the movement of particles or changes in particle diameter as the intensity of light with time.

The evaluation was made according to the following criteria.

A: No sedimentation phenomenon was observed even after the elapse of 2 weeks.

B: A sedimentation phenomenon was observed after the elapse of 2 weeks.

[0143]

#### Evaluation 4: Print Density

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). A solid print was made on Xerox P paper (manufactured by Xerox Corp.) of plain paper. The density of this solid print portion was measured with a spectrophotometer (GRETAGA SPM-50, manufactured by Gretag Macbeth GmbH). The results thus obtained were evaluated according to the following criteria.

A: The OD value of the color ink is 1.2 or more.

B: The OD value of the color ink is 1.15 to less than 1.2.

C: The OD value of the color ink is less than 1.15.

[0144]

#### Evaluation 5: Print Quality

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). Twenty-four capital letters and 24 lowercase letters of the alphabet were printed on each plain paper (partly including recycled paper) described below, visually observed and evaluated according to the following criteria.

AA: No blurring occurs on all papers.



A: The occurrence of slight blurring is only observed on 2 or 3 papers.

B: The occurrence of slight blurring is observed on all papers.

C: Much blurring occurs on all papers.

Print papers used for the evaluation are 12 papers of Conqueror, Favorit, Modo, Rapid Copy, EPSON EPP, Xerox P, Xerox 4024, Xerox 10, Neenha Bond, Ricopy 6200, Yamayuri (recycled paper) and Xerox R (recycled paper).

[0145]

#### Evaluation 6: Color Developability

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). A solid print was made on each of semi-glossy MC photo paper (manufactured by Seiko Epson Corporation) and Xerox P paper (manufactured by Xerox Corp.), and the  $C^*$  value of the solid print portion was measured. The ratio of the  $C^*$  value on the Xerox P paper (manufactured by Xerox Corp.) to the  $C^*$  value on the semigloss MC photo paper (manufactured by Seiko Epson Corporation) was determined, and the color developability on plain paper was evaluated according to the following criteria:

A: 0.9 or more;

B: 0.8 to less than 0.9; and

C: Less than 0.8.

[0146]

#### Evaluation 7: Abrasion Resistance

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). A solid print was made in a region of 10 mm X 10 mm on a super fine glossy film designed for ink jet printing (manufactured by Seiko Epson Corporation) at a duty of 100%. After standing at a temperature of 25°C for 1 hour, the above-mentioned printed region was rubbed with a yellow highlight pen using an aqueous ink (ZEBRA PEN2 (trade name), manufactured by Zebra Pen Corporation) at a load of 500 g and at a speed of 10 mm/sec, and it was observed whether a stain occurred or not. The results thereof were evaluated according to the following criteria.

A: No stain occurs at all when the printed region was rubbed twice.

B: No stain occurs when the printed region was rubbed once, but a stain occurs when it was rubbed twice.

C: A stain occurs when the printed region was rubbed once.

[0147]

#### Evaluation 8: Water Resistance

One milliliter of ion exchanged water was dropped on the printed portion of the printed matter obtained in the print density test of evaluation 4. The state after 20 minutes was visually observed, and evaluated according to the following criteria.

A: No change occurs on all papers.

B: A colorant slightly bleeds out of the printed portion, but the recognition of letters is possible.

C: A colorant bleeds out of the printed portion to make the contours of printed letters unclear, so that the recognition of the letters is difficult.

[0148]

#### Evaluation 9: Ejection Stability

Each of the inks for ink jet recording of Examples and Comparative Examples was mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation), and 1-mm ruled lines were printed on super fine paper designed for ink jet printing (manufactured by Seiko Epson Corporation). The state of printing such as dot missing and deviation in ink landing position was visually observed, and evaluated according to the following criteria.

A: Even when 10,000 or more prints are carried out, neither dot missing nor deviation from the ink landing

position occurs.

B: When 1,000 to less than 10,000 prints are carried out, dot missing or deviation from the ink landing position occurs.

C: When 100 to less than 1,000 prints are carried out, dot missing or deviation from the ink landing position occurs.

D: When less than 100 prints are carried out, dot missing or deviation from the ink landing position occurs.

[0149]

#### Evaluation 10: Clogging Reliability

After the printing conducted in the above-mentioned evaluation 5, a power supply of the printer was turned off, and the ink was allowed to stand. After one week, the same printing test was conducted. The "state of ink ejection" at that time was visually observed, and evaluated according to the following criteria.

A: Normal printing starts without a cleaning operation at the same time that print signals are transmitted to the printer.

B: Normal printing is conducted after three or less cleaning operations.

C: Normal printing is conducted after six or less cleaning operations.

D: Normal printing cannot be conducted even when a

cleaning operation is repeated seven or more times.

[0150]

Evaluation 11: White Blank

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). A solid print was made on each plain paper used in evaluation 5. This solid print portion was visually observed, and evaluated according to the following criteria.

A: Fine portions in which the ink does not spread on the solid print portion to cause the original color of the paper to appear (referred to as white blanks in this specification) are not observed at all.

B: Fine portions in which the ink does not spread on the solid print portion to cause the original color of the paper to appear are slightly observed.

C: Fine portions in which the ink does not spread on the solid print portion to cause the original color of the paper to appear are observed.

D: Fine portions in which the ink does not spread on the solid print portion to cause the original color of the paper to appear are observed in large numbers.

[0151]

[Table 7]

	Evalua tion 1-1	Evalua tion 1-2	Evalua tion 2	Evalua tion 3	Evalua tion 4	Evalua tion 5	Evalua tion 6	Evalua tion 7	Evalua tion 8	Evalua tion 9	Evalua tion 10	Evalua tion 11
	Dispersi bility 1	Disper sibility 2	Disper sion Stab ility	Sediment ation Prop erties	Print Density	Print Quality	Color Devel opability	Abrasi on Resist ance	Water Resis tance	Ejecti on Stab ility	Cloggi ng Reliab ility	White Blank
Example 1	A	A	A	A	AA	A	A	B	A	A	A	A
Example 2	A	A	A	A	AA	A	A	B	A	A	A	A
Example 3	A	A	A	A	AA	A	A	B	A	A	A	A
Example 4	A	A	A	A	AA	A	A	A	A	A	A	A
Example 5	A	A	A	A	AA	A	A	A	A	A	A	A
Example 6	A	A	A	A	AA	A	A	A	A	A	A	A
Example 7	A	A	A	A	AA	A	A	B	A	A	A	A
Example 8	A	A	A	A	AA	A	A	A	A	A	A	A

[0152]

[Table 8]

	Evalua tion 1-1	Evalua tion 1-2	Evalua tion 2	Evalua tion 3	Evalua tion 4	Evalua tion 5	Evalua tion 6	Evalua tion 7	Evalua tion 8	Evalua tion 9	Evalua tion 10	Evalua tion 11
	Disper sibili ty 1	Disper sibili ty 2	Dispersi on Stabilit y	Sediment ation Properti es	Print Densit y	Print Qualit y	Color Develo pabili ty	Abrasi on Resist ance	Water Resist ance	Ejecti on Stabil ity	Cloggi ng Reliab ility	White Blank
Com. Ex. 1	B	B	B	A	C	C	-	B	A	B	C	C
Com. Ex. 2	A	A	A	A	C	C	B	B	A	A	B	C
Com. Ex. 3	A	A	A	A	C	C	B	B	A	A	B	C
Com. Ex. 4	A	A	A	A	C	C	B	B	A	A	B	C
Com. Ex. 5	C	C	C	B	B	C	-	A	A	C	C	C
Com. Ex. 6	B	B	B	A	B	C	B	A	A	B	C	C
Com. Ex. 7	C	C	C	B	B	C	B	A	A	C	C	C
Com. Ex. 8	B	B	B	A	B	C	B	A	A	B	C	C
Com. Ex. 9	A	A	A	A	A	C	B	A	A	B	C	C
Com. Ex. 10	A	A	A	A	A	A	-	C	A	A	A	A
Com. Ex. 11	A	A	A	A	A	A	A	C	A	A	A	A
Com. Ex. 12	A	A	A	A	A	A	A	C	A	A	A	A
Com. Ex. 13	A	A	A	A	A	A	A	C	A	A	A	A

[0153]

[Table 9]

	Evalua tion 1-1	Evalua tion 1-2	Evalua tion 2	Evalua tion 3	Evalua tion 4	Evalua tion 5	Evalua tion 6	Evalua tion 7	Evalua tion 8	Evalua tion 9	Evalua tion 10	Evalua tion 11
	Dispersi bility 1	Disper sibili ty 2	Disper sion Stabil ity	Sedime ntatio n Proper ties	Print Densit y	Print Qualit y	Color Develo pabili ty	Abrasi on Resist ance	Water Resist ance	Ejecti on Stabil ity	Cloggi ng Reliab ility	White Blank
Com. Ex. 14	D	D	D	B	C	C	-	C	B	D	D	D
Com. Ex. 15	D	D	D	B	C	D	-	C	B	D	D	D
Com. Ex. 16	D	D	D	B	C	D	C	C	B	D	D	D
Com. Ex. 17	D	D	D	B	C	C	C	C	B	D	D	D
Com. Ex. 18	D	D	D	B	C	D	C	C	B	D	D	D
Com. Ex. 19	B	B	B	A	C	D	-	B	B	B	C	C
Com. Ex. 20	A	A	A	A	C	D	C	C	B	B	C	C
Com. Ex. 21	A	A	A	A	C	D	C	B	B	B	C	C
Com. Ex. 22	A	A	A	A	C	D	C	C	B	B	C	C
Com. Ex. 23	C	C	C	B	B	D	-	-	B	D	D	C
Com. Ex. 24	C	C	C	B	B	D	B	C	B	D	D	C
Com. Ex. 25	C	C	C	B	B	D	B	B	B	D	D	C
Com. Ex. 26	C	C	C	B	B	D	B	C	B	D	D	C



[0154]

As shown in Tables 7 to 9, the inks for ink jet recording of Examples were excellent in all evaluation items.

In particular, the solid wetting agent-containing inks for ink jet recording of Examples 1 to 8 and Comparative Examples 24 to 26 showed good results in clogging reliability.

The inks for ink jet recording of Comparative Examples 14 to 18 obtained by dispersing the pigments with the dispersants were insufficient in dispersibility, dispersion stability, print density, print quality, color developability, abrasion resistance and ejection stability. The inks for ink jet recording of Comparative Examples 1 to 4 and 19 to 22 in which the conventional microencapsulated pigments were used as colorants and the concentration of the microencapsulated pigments was set to a value lower than that of the inks of Examples were excellent in dispersion stability and ejection stability, but failed to obtain sufficient results for print density, print quality, abrasion resistance and color developability, the evaluations to the resulting recorded matter.

On the other hand, the inks for ink jet recording of Comparative Examples 5 to 8 and 23 to 26 in which the

above-mentioned conventional microencapsulated pigments were used as colorants and the concentration of the microencapsulated pigments was set to a value equivalent to that of the inks of Examples were particularly poor in dispersibility, dispersion stability and ejection stability. Further, the inks for ink jet recording of Comparative Examples 9 to 13 containing the surface-treated pigments as the colorants were excellent in dispersion stability and ejection stability, but poor in abrasion resistance.

[0155]

[Advantages of the Invention]

As described above, according to the microencapsulated pigment and the process for preparing the same according to the invention, there can be provided a microencapsulated pigment capable of preparing an ink for ink jet recording satisfying all the following (1) to (6) and a process for preparing the same, and an aqueous dispersion.

- (1) Excellent in dispersion stability;
- (2) Excellent in ejection stability from a recording head;
- (3) Capable of obtaining recorded matter excellent in fastness of images;

(4) Capable of obtaining recorded matter excellent in print density of images;

(5) Capable of obtaining recorded matter excellent in abrasion resistance of images; and

(6) Capable of obtaining recorded matter in which images are hard to blur, and which is excellent in color developability of images, even when plain paper is used as a recording medium.

[0156]

Further, according to the ink for ink jet recording of the invention, there can be provided an ink for ink jet recording satisfying all the following (1) to (6):

(1) Excellent in dispersion stability;

(2) Excellent in ejection stability from a recording head;

(3) Capable of obtaining recorded matter excellent in fastness of images;

(4) Capable of obtaining recorded matter excellent in print density of images;

(5) Capable of obtaining recorded matter excellent in abrasion resistance of images; and

(6) Capable of obtaining recorded matter in which images are hard to blur, and which is excellent in color developability of images, even when plain paper is used as a recording medium.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a schematic view showing a state in which pigment particles having an anionic group on the surface thereof are dispersed in an aqueous medium and coexist with a cationic polymerizable surfactant and an anionic polymerizable surfactant.

[Fig. 2] Fig. 2 is a schematic view showing a state in which the cationic polymerizable surfactant and the anionic polymerizable surfactant are polymerized in the dispersed state shown in Fig. 1:

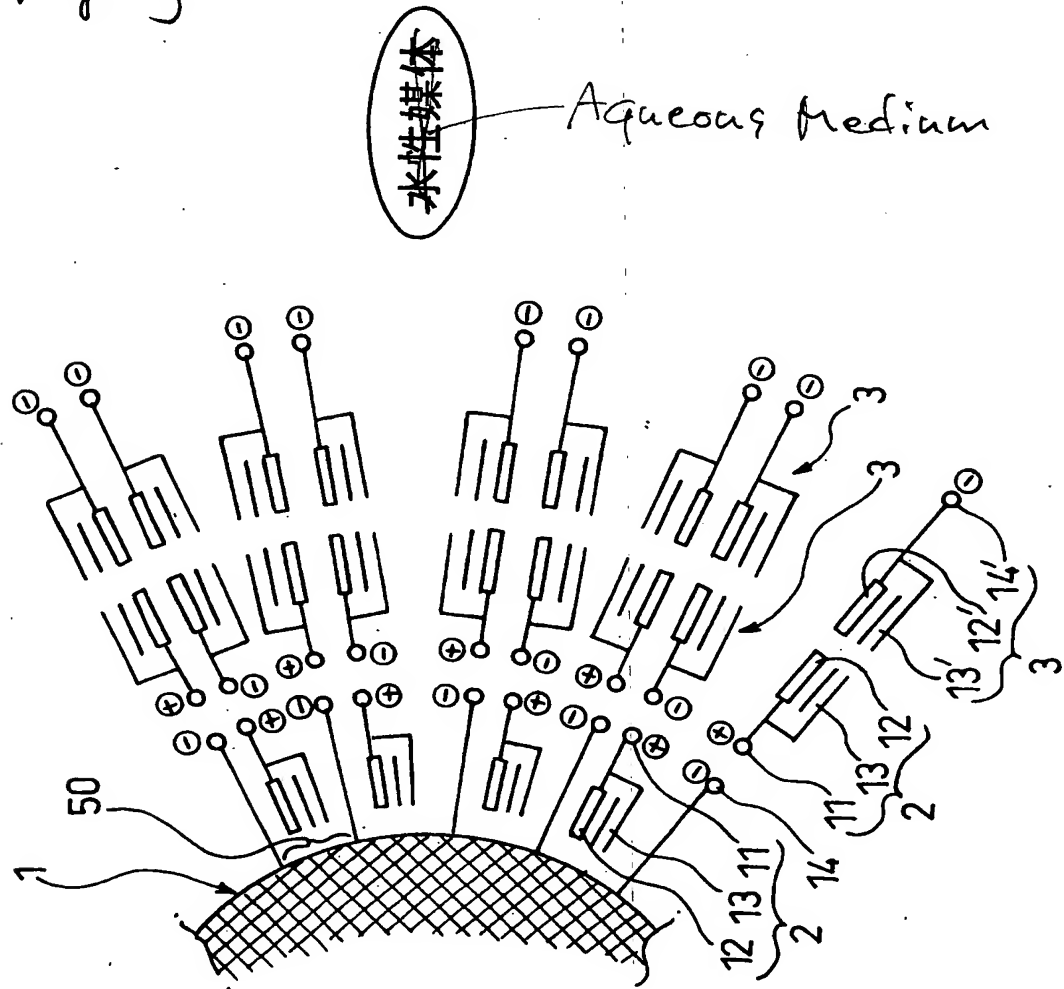
[Description of Reference Numerals and Signs]

- 1: PIGMENT PARTICLE
- 2: CATIONIC POLYMERIZABLE SURFACTANT
- 3: ANIONIC POLYMERIZABLE SURFACTANT
- 10: HYDROPHILIC GROUP
- 11: CATIONIC GROUP
- 12, 12': HYDROPHOBIC GROUP
- 13, 13': POLYMERIZABLE GROUP
- 14, 14': ANIONIC GROUP
- 60: POLYMER LAYER (POLYMER)
- 100: MICROENCAPSULATED PIGMENT

【書類名】 図面 [Designation of Document] Drawings

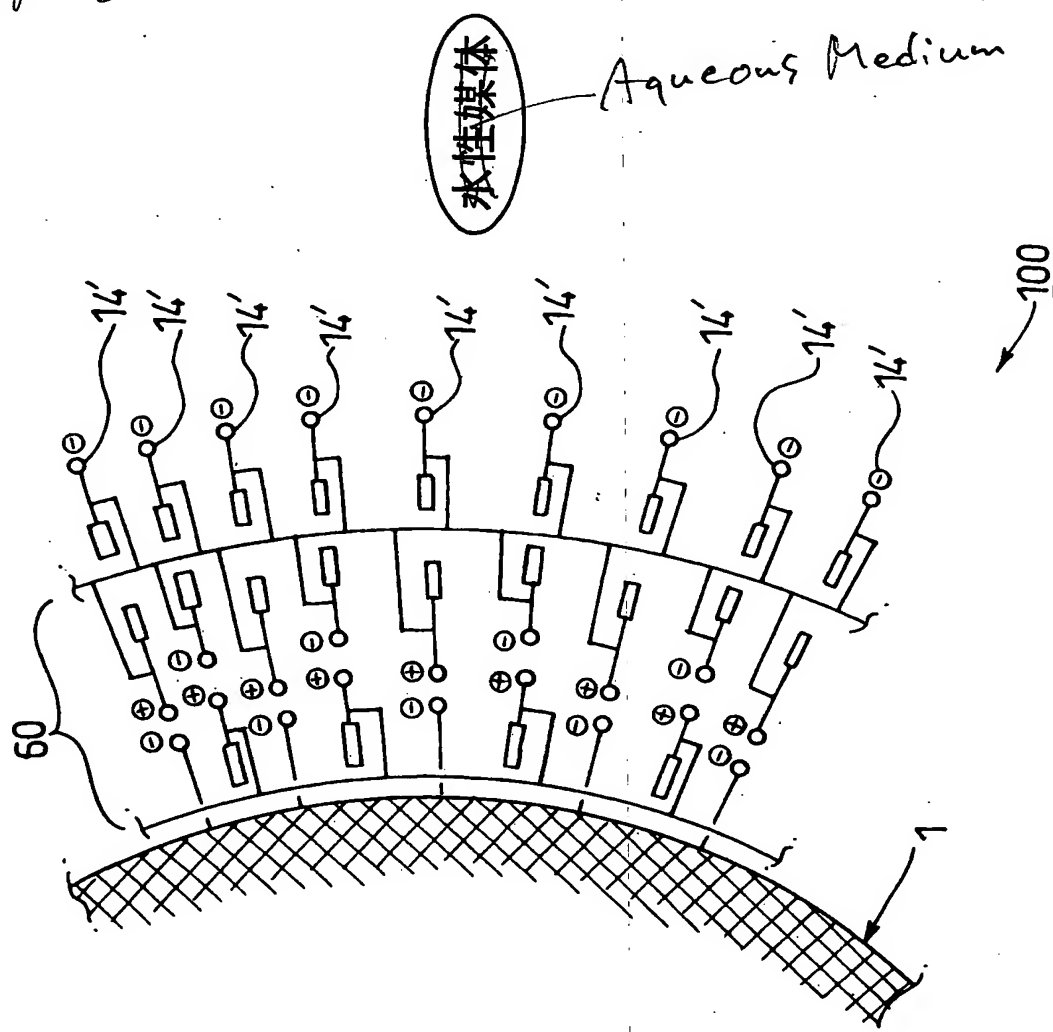
【図1】

[Fig. 1]



【図2】

[ Fig 2 ]



[Designation of Document] ABSTRACT

[Abstract]

[Task] To provide a process for preparing a microencapsulated pigment, a microencapsulated pigment (MCP), and an aqueous dispersion which can prepare an ink for ink jet recording (IJI), which is excellent in dispersion stability, excellent in ejection stability, excellent in fastness, excellent in print density, and excellent in abrasion resistance so as to provide a recorded matter in which images hardly blur and to provide the IJI.

[Means for Resolution] Provided are a process for preparing an MCP, which comprises adding a polymerizable surfactant having a hydrophilic group, a hydrophobic group and a polymerizable group, a polymerization initiator and an aqueous medium to a wet pigment, and conducting emulsion polymerization to encapsulate pigment particles with a polymer, an MCP obtained using the process for preparing an MCP, and an IJI containing at least the MCP and water.

[Selected Drawing]

None